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PROCEEDINGS: FIRST JOINT SYMPOSIUM ON DRY SO_2 AND SIMULTANEOUS SO_2/NO_X CONTROL TECHNOLOGIES

Volume 1. Fundamental Research and Process Development

Symposium Cochairpersons:
M. W. McElroy (EPRI) and R. D. Stern (EPA)

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Mountain View, CA 94039

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16. ABSTRACT

The proceedings document the First Joint Symposium on Dry SO2 and Simultaneous SO2/NOx Control Technologies, held November 13-16, 1984, in San Diego, CA. The symposium, sponsored jointly by EPRI and EPA, was the first meeting of its kind devoted solely to the discussion of emissions control processes based on dry injection of calcium or sodium sorbents to meet SO2 and NOx regulations for coal-fired power plants. Processes that were discussed included: direct furnace injection of calcium-based sorbents, sorbent injection combined with low-NOx burners for simultaneous SO2/NOx control, and post-furnace injection of calcium and sodium sorbents. The symposium provided a timely forum for the exchange of data and information on the current status and plans for these emerging technologies. The presented papers began with a keynote address on acid rain strategies and control technology implications, followed by overviews of EPRI, EPA, and Canadian programs and the utility perspective for dry control technologies. Other papers focused on the latest advances in fundamental research and process design, power plant integration and economics, field applications, and full-scale testing. In addition to the U.S. and Canada, attendees represented West Germany, France, The Netherlands, Austria, and Japan.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
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Nitrogen Oxides	Coal	Stationary Sources	07B	21D
Sulfur Dioxide	Combustion	Dry SO_2 Control		21B
Sorbents	Economics	Simultaneous SO_2/NO_x Control	11G	05C
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ABSTRACT

Forty six papers describing recent advances in dry sorbent injection technologies for SO_2 control were presented at the 1st Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies. These papers covered the following topics: fundamental research; pilot-scale development of furnace injection; burners for simultaneous SO_2/NO_x control; post-furnace SO_2 removal; process integration and economics; sorbent availability and costs; and field applications and full-scale testing.

PREFACE

The 1st Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies was held November 13 through 16, 1984 in San Diego, California. This symposium, jointly sponsored by EPRI and EPA, was the first meeting of its kind devoted solely to the discussion of emissions control processes based on dry injection of calcium or sodium sorbents to meet SO_2 and NO_x regulations for coal-fired power plants. Specific processes that were discussed included: direct furnace injection of calcium-based sorbents, sorbent injection combined with low-NO_x burners for simultaneous SO_2/NO_x control, and post-furnace injection of calcium and sodium sorbents. The objective of the symposium was to provide a timely forum for the exchange of data and information on the current status and plans for these emerging technologies.

Forty six papers were presented beginning with a keynote address on acid rain strategies and control technology implications, followed by overviews of the EPRI, EPA, and Canadian programs, and the utility perspective for dry control technologies. Other papers focused on the latest advances in fundamental research and process design, power plant integration and economics, field applications, and full-scale testing. A panel of representatives from architect-engineering firms, boiler manufacturers, and utility companies discussed the impact of dry SO_2 control processes on new and existing power plants.

The speakers included EPRI and EPA staff members as well as representatives from utility companies, manufacturers of utility boilers and process equipment, sorbent suppliers, and research and development groups conducting investigations sponsored by EPRI, EPA, and others. **Participants from West Germany, France, The Netherlands,** Austria, Canada, and Japan provided a worldwide update on technological developments and an international perspective on SO_2 and SO_2/NO_x control issues.

The Cochairmen of the symposium were Michael W. McElroy, Subprogram Manager of EPRI's Air Quality Control Program in the Coal Combustion Systems Division and Richard D. Stern, Chief of EPA's LIMB Applications Branch of the Industrial Environmental Research Laboratory.* The welcoming address was given by John Hamrick, Vice President of Customer Service for San Diego Gas & Electric and the keynote address was given by Donald J. Ehreth, Deputy Assistant Administrator, Office of Research and Development, EPA.

The symposium proceedings has been published in two volumes:

- Volume 1: Fundamental Research and Process Development

  -- Session I: Introduction
  -- Session II: Fundamental Research
  -- Session III: Pilot-Scale Development of Furnace Injection
  -- Session IV: Burners for Simultaneous SO_2/NO_x Control
  -- Session V: Post-Furnace SO_2 Removal

(*) Now, the Air and Energy Engineering Research Laboratory.

- Volume 2: Power Plant Integration, Economics, and Full-Scale Experience

  -- Session VI: Process Integration and Economics
  -- Session VII: Sorbent Availability and Costs
  -- Session VIII: Field Applications and Full-Scale Testing

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SESSION I: INTRODUCTION

Chairman, Richard Stern, EPA, IERL/RTP and Michael McElroy, EPRI

ACID DEPOSITION STRATEGIES AND IMPLICATIONS FOR CONTROL TECHNOLOGY REQUIREMENTS

Donald J. Ehreth
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Washington, DC 20460

It is really a pleasure for me to be here today. My pleasure stems principally from the importance of the topic we have assembled here to discuss, acid deposition.

I would like to begin by describing my personal introduction to the topic, so you can get a better feel for the factors that have guided EPA's interest in acid rain control. Then, I plan to bring you up to date on the history of the work going on to help solve the problem. I'll close my talk with just enough details of some of the presentations that are before us to whet your appetite and prepare you to consider several approaches to solutions being considered by both EPA and the remainder of the engineering research community, both here and abroad.

Although EPA and the other involved segments of the scientific community had already expressed considerable concern about the effects of acid deposition, my involvement peaked about July 27, 1983, when, as Director of the Office of Environmental Engineering and Technology (OEET), I was asked to convene a panel of experts representing industry, boiler manufacturers, engineering firms, academia, research consulting firms, public policy groups, the power industry, burner manufacturers, manufacturing and chemical industry representatives, and (of course) EPRI.

Prompted by the receipt of $5 million from Congress in the Limestone Injection Multistage Burner (LIMB) area, we convened the panel of 19 people, many of whom are here with us today. I asked the panel three questions:

(1) Is the relative emphasis between the LIMB research and development program, and the wall-fired boiler LIMB demonstration project as envisioned by EPA appropriate?

(2) Is the LIMB demonstration feasible within the timeframe proposed by EPA? (EPA proposed that a design manual be available by 1988 so that "somebody" can put this thing on the street after its being demonstrated at a reasonable boiler size.)

(3) What is the probability of a successful LIMB demonstration?

At that time, public interest regarding acid rain had been steadily growing. Congress was interested. Congress was active. Congress was excited. Many bills (no less than 15 of which specified some degree of emission reduction, to indicate an opening for control technology solutions) were floating through Congress. EPA's LIMB program at that time was focused on research and development, leaving the demonstration and commercialization to the private sector. Basically, we were going to turn over EPA's prototype and pilot plant data to the private sector, which would then assume the responsibility for commercialization. That is, in fact, the philosophy of the Administration: to encourage the private sector to commercialize solutions to pollution problems, as well as other problems facing the nation.

EPA laid out very ambitious goals for both degree of removal and cost for LIMB. We had established a goal of 50 to 60 percent reductions of SO_2 and NO_x for retrofit systems. We were estimating capital cost savings of 70% and overall cost savings of up to 50% for LIMB vs state-of-the-art flue gas desulfurization technology. Someone had asked if the claims were valid. Were they figments of our imagination, or were they real? That's why we convened the panel. We asked them to help us. They were unbiased. They had nothing to gain or lose from the exercise. I was delighted to work with such a fine group. They were candid. It was a one-day session. No one left until the final "gong." From my perspective, it was an incredibly successful venture.

Following the panel meeting, I wrote a summarizing report. Let me summarize the panel's comments responding to the three questions I asked initially.

Question 1: Appropriateness of the relative emphasis between LIMB research and development and the demonstration project envisioned by EPA: Of the panel, 37 percent supported the proposed approach; the balance split almost equally between more research and development emphasis (21 percent) and more demonstration (26 percent). Three panelists (15 percent) did not express any clear-cut opinion.

Question 2: Feasibility of the demonstration within the proposed timeframe: All panelists supported the need for at least one demonstration to prove the technology. Many questioned the adequacy of a single demonstration to cover all boiler/size variables. That the schedule should be at least as fast as that proposed by EPA was supported by 69 percent of the panel. Some of those attending saw 1990 as looming on the horizon, and 1988 as a bit too tight. Most (53 percent) of the panelists agreed that EPA's schedule was fairly reasonable. Some favored delaying the schedule for a year or two. In fact, between 16 and 26 percent of the group favored delays in place of any acceleration at all. In brief, there was a broad range of opinions on this question; however, for the most part, the panel concurred with EPA's proposed schedule.

Question 3: The probability of success, defined as 50 percent SO_2 removal using high sulfur coal within 3 years: Nearly three-quarters of the panelists indicated a 50/50 probability of success, with estimates ranging as high as 70/30. Although 21 percent of the panel did not express a quantitative opinion, no strongly negative opinions were expressed. In fact, several panelists were quite positive concerning the potential of the technology.

The panel's conclusions followed an elaborate in-depth presentation of EPA's latest data. In fact, some of the data had just been generated the day before, and presenters were arranging graphics and drawing conclusions on the plane from the West Coast the night before.

Something interesting happened at the meeting, something that we hadn't anticipated, but something that led to bigger and better things. In addition to answering the three questions posed by EPA, the panelists evidenced interest in a presentation by the Southern Company/EPRI program. Southern's research favored an intermediate step of using a 20- to 80-MW boiler in the research and development before the demonstration. Nearly 40 percent of the panelists recommended this approach be considered, although individual views varied significantly. In other words, many people thought that EPA's proposed demonstration timeframe was acceptable, but suggested adding a smaller unit before the final demonstration.

A number of the panelists expressed the need for close communication and coordination between EPA and EPRI. In the past, they said, these organizations have met informally and infrequently on LIMB. The need for a more formal mechanism was apparent: the Office of Management and Budget (OMB) seemed to know what each of us was planning to do. We'd meet with OMB; they'd tell us what EPRI was doing. EPRI would meet with OMB; they'd tell them what EPA was doing. But although there was communication at the working level we never formally got to the same table at the same time. Furthermore, although neither of us had claimed all the technical expertise available to solve the SO_2/NO_x control technology program, many of us thought that (collectively) we could go a long way to develop sensible, technically feasible, and cost effective solutions to the mounting public issue.

George Green, whom you will hear from in just a little while, told me recently what had to be done. George told me unhesitatingly that there just wasn't enough money for EPRI and EPA to work independently. He said that there had to be a way for EPA and EPRI to pool resources and work together. The bottom line was that EPA and EPRI did get together and, I believe, both learned to value compromise and cooperation.

We are testing a smaller boiler than EPA had originally intended to test. This option was strongly supported by EPRI and others in the July 1983 meeting. Frankly, we at EPA did not support it at that time. Furthermore, out of that meeting grew a joint steering committee for field projects and collection of information on foreign technology and demonstrations. We are developing a cooperative research agenda. We have technical coordination and information exchange meetings every 6 months (two of which have already been held). I believe that this symposium is a manifestation of EPRI's and EPA's joint commitment to respond to the acid rain issue with sensible, technically sound, and cost-effective research strategies.

EPRI and EPA both support these goals; and today's attendance shows that we are not alone. The problems are many and there is enough room here for all of us, but let's continue to share needs, goals, research status, discussion of technical issues and, most importantly, technology transfer. It is no secret to us, the air pollution control technology professionals, that the nation's attention has been focused on acid rain policy discussions within Congress and the Executive Branch for the past several years. For this symposium to focus on that debate would be a major loss of time and talent. Let's continue to focus on technical issues. If and when Congress passes legislation that is signed by the President, the clock starts ticking and the hour of crisis begins. That's been the experience in the past; and the future should be the same.

The theme of today's conference is to continue what has been started. At that meeting in July 1983, the attendees (not just EPA) got a glimpse of EPRI's and industry's plan; however, only a few participants at that meeting presented real data or plans relating to their own LIMB-like control technology. Things have changed since then. We are building on a spirit of cooperation, born in 1980 and 1981 when we (EPRI and EPA) began to jointly sponsor FGD and NO_x control technology symposia, and to jointly fund projects to improve electrostatic precipitators (ESPs).

EPA recently implemented the State Acid Rain (STAR) Program. It is an attempt at contingency planning, an attempt at front-end planning and analysis of issues which could flow from an acid rain control program if one is enacted. STAR will focus exclusively on management and administrative problems and solutions. Research needs might flow from it, but definition of research needs is the problem for us and the Interagency National Acid Rain Program. The National Acid Rain Program is aimed at establishing the scientific underpinning for the cause and effect (or source-receptor) debate. The control technology research effort might also be considered contingency planning, and that's why the government has research in LIMB, coal cleaning, fluidized bed furnaces, and other areas.

The various acid deposition bills that were introduced in the 98th Congress included approximately 15 measures which required emission reductions. At this time, I am not sure of what legislation will be introduced by the new Congress, what it will contain, nor do I want to speculate. As I said before, that is not the purpose of this conference. It is sufficient to say that the issue will appear again. Let's assume that the fundamental feature, emission reduction, will remain. Therefore, research in this area continues to be appropriate. Congress obviously feels strongly: they appropriated $5 million in 1984; in 1985 they gave us an additional $6.5 million; and with that money we plan to demonstrate wall-fired boilers and set the stage for demonstrating tangentially fired boilers. LIMB technology, if fully developed to our expectations, would be uniquely suited to take advantage of a flexible control implementation plan. Assuming that simultaneous SO_2 and NO_x controls would be allowed, LIMB, at a 2 to 1 NO_x/SO_2 tradeoff, would afford a very attractive cost benefit. We would project that LIMB would be considered equivalent to 70% percent efficient FGD if it achieved 60 percent reductions of both SO_2 and NO_x, or equivalent to a 60 percent efficient FGD if it obtained only 50 percent control of each pollutant.

During the next few days, you will hear over 45 papers on all aspects of dry SO_2 and simultaneous SO_2 and NO_x controls. The topics include, fundamental research stressing process chemistry and sorbent, gas mixing, pilot-scale development, the burner configuration for NO_x and SO_2 removal, post-furnace SO_2 removal, and sorbent availability and cost which, by the way, can account for 20 to 50 percent of projected annual revenue requirements. You will hear about field application and testing. You'll hear about key research findings.

For example, we feel that sufficient data are already available for proof of concept. There is a very narrow window establishing efficiency at somewhere between 1600 and 2300°F (871 and 1260°C) and sorbents should not be exposed to higher temperatures. The residence time in that temperature window is extremely short, perhaps less than 1 second. Therefore, mixing is critical. We found out recently that we probably would require high surface area sorbents to meet and possibly exceed our performance goals. Because of the ever-present potential for slagging or fouling or ESP loading or overloading, high surface area sorbents offer the possibility to reduce the need to add significant quantities of solids. However, there is always some good news accompanying such warning: you'll be hearing that the impact of sorbents is manageable. Full-scale demonstrations will also be discussed, all completed recently or on-going both in the domestic and foreign scene: DOE's project, Conoco's project, and projects in Germany, France, Canada, and Austria. And I know that we have visitors here from Sweden, Japan, and other countries.

These few days of exchange can bring all of us to the same level of understanding and knowledge. Then we can move on toward achieving a consensus on the remaining problems and, finally, agree on the R&D that is needed. This is essential; as George Green has said, "there just isn't enough money to go around." Supportable performance and cost data are needed if this technology is to be factored into planning. Industry and government have a unique opportunity to work together as we've already started to do. I especially applaud the organizations of this symposium who assembled this group and who did the leg work, the hard work, and the late night work to put it together. And last, but not least, I draw special attention to those participants from Germany, France, Canada, and Austria. I look forward to the results of this outstanding display of cooperation and am proud to have played even a small role in it.

THE EPRI PROGRAM -- BACKGROUND AND MOTIVATION

John S. Maulbetsch
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Good morning and welcome on behalf of EPRI to this 1st Joint Symposium on Dry SO_2 Control and Simultaneous SO_2/NO_x Control Technologies. It is a pleasure for us to participate in this conference with EPA and to continue the tradition of giving joint attention to important technologies for air quality control. I think this conference may be rememberd as a landmark session in that it is the first of its type devoted to just these particular technologies. As Mike McElroy noted while introducing me, I am new to this research area. So to the degree that these are emerging technologies, I guess I might be described as an emerging technologist.

My charge this morning is to give EPRI's perspective on these dry control options. To begin, let me say that there is clearly a fundamental benefit to having a variety of approaches to any particular problem. One of the obvious characteristics of the electric utility industry is its diversity. Across the industry, there is a diversity of financial situations; a diversity of regulations that have to be contended with; a diversity of fuels, sizes of plants, ages of plants, availability of water resources, availability of space for the management of solid byproducts; and a diversity in the degree to which each utility is prepared to accept the risks of technological innovation. Therefore, when you pose the question, for example, of how to deal with acid rain related pollution control requirements, you get, as you would expect, a great diversity of opinion. No one solution need be universally preferred at all times and in all places in order to be useful. But each potential solution does have to have a niche, and one of the things that we have to be attentive to as we do our research is identification and characterization of these niches. SO_2 control can be achieved in many ways -- from plant retirement to fuel switching, fuel blending, fuel cleaning, or flue gas treatment -- and the technolgoies we are considering here today, particularly furnace sorbent injection, are fundamentally different ways. Personally, I think furnace sorbent injection is an especially attractive approach in that it represents intervention in the process of power production to control pollutants at the point of their liberation or formation. This represents another strategy in the arsenal of technologies available to the industry.

If there is a theme to my remarks today, it is that dry SO_2 control and simultaneous NO_x/SO_2 control have been and still are grounded in perceptions. As our research continues, this is changing of course. But, whether this change is coming as rapidly as the forces which may lead to decisions to implement the technologies is not entirely clear. Decisions to implement are coming fast upon us, and they may have to be made without all the facts in hand. If so, they will necessarily be made on the basis of current perceptions.

One important perception is that these technologies are simple and inexpensive. Now that's bound to be a plus. They represent, I think, a part of a trend away from end-of-the-pipe technologies that are perceived as complicated and expensive. I have a colleague at EPRI in the health effects group who in a previous incarnation was involved in a massive survey of health care services in the United States and around the world. Emphasis in the survey was on the relationship between levels of health care and economic welfare. After several years, several million surveys, and the expenditure of a great deal of money, the survey team held a press conference to reveal its finding. The finding can be summed up in one sentence: "It is better to be well and rich than to be sick and poor." I guess the technological equivalent of that is that it is better to be simple and inexpensive than to be complicated and costly. Technological simplicity, however, implies more than just conceptual or mechanical simplicity. It implies in some sense an absence of risk, or at least an understanding of the risks involved, and a sense that you are not buying into problems that are not obvious from the beginning.

As to the perception of low cost, I think there is general agreement that these technologies represent a substantially reduced first cost. However, the degree to which they represent a reduced total cost depends strongly on the performance expectations you hold for them and what you think you are going to need to do to reduce whatever uncertainties and risks that are associated with them. So there are some countervailing concerns, and some of these concerns are based on historical experience with technologies which were less than completely satisfactory. In this vein, Mr. Stern spoke earlier about being a born-again dry injection technologist, and harped back to the experience in the 1960's at TVA's Shawnee plant where dry injection did not perform as well as might have been anticipated, and where the effect on the boiler was less favorable than anticipated.

A moment ago I talked about risk, and how simplicity might be interpreted as implying an absence of risk, or certainly of reduced risk. This is not to say there are no strong perceptions of risk with these technologies, however. For example, there is the risk of whether the results we are seeing at the bench scale and the pilot scale can be achieved at full scale. If the achievable performance at larger scale is less than expected, then the economics of the process get called into question. There is also the risk of exacerbating particulate control problems by adding large quantities of additional material which must be taken out in particulate control devices. This concern is especially critical in retrofit situations.

Another risk is that the generation of solid byproducts of a different physical and chemical composition may make waste management both in and outside the plant more difficult. Finally, and specifically with furnace sorbent injection, there is the risk of fouling the boiler by intervening directly in the combustion and heat transfer process.

Given these considerations, these perceptions, what then has been and is EPRI's attitude toward these technologies? In a word, they clearly look like they are worth a shot. If the risk can be dealt with -- and as we proceed with our work I think we are coming close to the conclusion that they can be dealt with -- then the hoped-for results look well worth the effort of an intensive research, development, and demonstration program.

To take furnace injection as an example, let me give you a bit of the history and scope of our EPRI research effort. We started off 2 or 3 years ago with some proof of concept work in conjunction with MHI on a tangentially fired pilot-scale boiler in Japan. This work was done at a modest scale, but it confirmed the expectation that performance was good. We moved from there to more general bench-scale work in cooperation with Southern Company Services and Southern Research Institute. Here we tried to learn more about the fundamentals of the process -- where one ought to do the injecting, what one ought to do with regard to the choice and preparation of the sorbents, and what temperature was appropriate. At the same time this was going on, similar rekindling of interest was going on at EPA and elsewhere. In mid-1983, we tried to bring the programs together in a formal way, and in the course of doing that we all learned some things. We learned more about performance and what governs it, we learned more about where to inject the reagent, about how you go about choosing the reagent, and about how you go about preparing the reagent. We have learned something, I think, about the relationship between the injection process and the combustion process, and about the mixing in the postcombustion region that gives us yet a better chance for success. Probably the most significant question remaining is the risk associated with the boiler. In this regard, we and others will be continuing to work at the bench scale and at the pilot scale to learn more about the fundamental mechanisms involved, the hoped-for result being, of course, to increase our confidence and our ability to scale results up to large sizes.

We are also about to initiate a substantial program to look at waste management issues associated with these technologies as well as with atmospheric fluidized bed coal cleaning and other nonstandard coal combustion processes. Given that these technologies involve new, fundamentally different wastes, our goal is to see whether we are buyng into anything fundamentally different and more complex in the in-plant management of waste, its transport, containment, and the degree to which injection may affect the potential for waste utilization. We have seen waste utilization start to displace disposal for standard flyash, and it would be regrettable, I think, to somehow interrupt that trend by not being prepared for it.

Some of these issues can only be dealt with at the demonstration scale, so it is important to move as quickly as we can out of the laboratory and out of the pilot scale into field demonstration. It is with this in mind that we look forward to formal cooperation with EPA in its recently announced demonstration with Babcock & Wilcox and Ohio Edison. We are also looking vigorously right now for other demonstration opportunities. We think it is important to conduct demonstrations in a variety of situations using a variety of fuels and a variety of boiler types under a variety of utility operating conditions. So, we will be working hard over the next few months to identify some opportunities for this type of demonstration. We hope to have companion demonstrations to go along with the EPA work by perhaps 1986.

Many of my remarks here today, and those of previous speakers, have emphasized furnace injection. Part of my rationale for this is that I will be followed here in a few minutes by George Green who will talk in detail about backend, or baghouse injection of both sodium- and calcium-based sorbents. This technology is a little further along, really at the stage of commercialization, and we at EPRI have a sort of fatherly interest in it, having been associated with bringing it all the way from the laboratory to the commercial arena. Development of flue gas dry sorbent injection technology is almost a textbook example, I think, of what a well thought out research program and the cooperation of the right kind of parties can accomplish in a relatively short period of time.

Let me conclude simply by saying that there are a number of interesting technologies on the table here, all of which I think have a real potential to make a difference in the way the industry we serve does business. I am optimistic about their potential; I hope we are successful in achieving it; and I hope we have a good time in the process. I look forward to working with all of you in the years to come as we continue in this direction.

EPA's LIMB R&D PROGRAM - EVOLUTION, STATUS, AND PLANS

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ABSTRACT

The LIMB R&D program has provided a detailed understanding of the key processes governing sulfur capture with sorbents. While it appears that limestone alone will not achieve program goals, several other promising sorbents have been identified. Based on the R&D results and cost estimates use of these sorbents, LIMB shows substantial promise as a SO_x and NO_x control technology for retrofit applications. The ongoing R&D program should resolve the remaining technical questions and provide a basis for widespread private sector commercialization.

This paper provides a brief history of sorbent injection technology, synopsizes the status of LIMB R&D, and discusses future program plans.

INTRODUCTION

The EPA is developing Limestone Injection with Multistage Burners (LIMB) as a potential low cost control technology for SO_x and NO_x, which are believed to be two of the major precursors of acid precipitation. The LIMB program is structured to provide an understanding of the controlling factors in the process and to establish a basis for private sector decisions on commercialization. The purpose of this paper is: 1) to provide a brief history of previous and other current sorbent furnace injection efforts; 2) to summarize the status of the LIMB program; and 3) to outline planned research and development. Most of the technical subjects discussed in this paper will be discussed in greater detail by other symposium presentations.

BACKGROUND

Sulfur oxides (SO_x) and nitrogen oxides (NO_x) are two major pollutants resulting from the combustion of fuels. Coal fired utility boilers account for about 70 percent of the SO_x and 20-25 percent of the NO_x emissions in the United States. For the 180,000 MW of coal fired boiler capacity east of the Mississippi River, this amounts to approximately 16 million tons* of SO_2 and 4-5 million tons of NO_x per year. Only about 10 percent of these boilers are subject to NSPS controls for SO_x and NO_x. Therefore to accomplish any significant reduction in SO_x and NO_x requires a retrofit of existing boilers which may have a remaining useful life of from 5 to 30 years. The vast majority of these are wall-fired and tangentially fired boilers.

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* 1 Ton = 907 kg

The seriousness of the acid rain problem and the importance of various acid precursor sources are still under debate; however, control of SO_2 from utility boilers is a major element in all proposed strategies. In addition NO_x is increasingly being linked to forest damage mechanisms. Proposed reductions of SO_2 range from 5 to 12 million tons per year, and the issue of an NO_x offset is being debated.

Control Technology Options

The choice of emission control strategies will have a significant effect not only on the ability to achieve any mandated reduction but also on its cost to the nation. The final decision on the technology mix will be based on the availability, specific performance, cost, and overall economic impact on the nation, including socioeconomic factors such as displacement in the work force. Among the choices commercially available are coal switching, coal cleaning, and various types of flue gas desulfurization (FGD) systems. In addition, some early analyses indicated that a low capital cost technology would be attractive even at moderate SO_2 removal (e.g., 50 percent control). Although there are several approaches being developed, none of the potential low cost alternatives have been demonstrated. One such rapidly emerging technology is LIMB which is based on injection of sorbents into the boiler for direct capture of SO_2 from the combustion gases.

History of Sorbent Injection

There is a considerable body of background information on sulfur capture by injection of sorbents into a conventional boiler. The information includes the experience in the U.S. with sorbent injection through a number of boilers in the late 1960's and early 1970's, some current experience in Germany on both brown coal boilers and other small-scale experimental facilities, and, finally, EPA testing using the distributed mixing low-NO_x burner with sorbent injection in a pilot-scale facility. This background section will present some of the details of each of these categories of experience.

U.S. Experience. In the late 1960's the National Air Pollution Control Administration (NAPCA, an EPA predecessor) and other organizations carried out a wide range of experimental work on sorbent injection for SO_x control. This was a part of the initial evaluation of the various technologies that might be viable for SO_x control where the control levels desired were from moderate to the maximum possible removal; i.e., on the order of 90 percent. The studies that were carried out involved both in-house work at NAPCA laboratories and contract work by boiler manufacturers and others. In addition to this, utilities, boiler manufacturers, and other organizations expended private resources examining the same technology. In general in these experiments the emphasis was on the injection of the sorbent into existing boilers separate from the coal and combustion air. The experience gained at this time covered a wide range of boiler designs including wall-fired units, tangentially fired units, and arch-fired units. The relative lack of success, compared to performance of FGD and the associated boiler operational problems, led to an end of the work at that time. While the conditions that we are examining at present are different than the conditions that existed in the late 1960's, it is worthwhile to consider the experience at that time.

NAPCA conducted a field evaluation program on a 150 MW boiler at the Shawnee Station of the Tennessee Valley Authority for the injection of limestone into the boiler. The limestone was injected into the radiant cavity of the boiler at a location above the top row of active burners. The reported data indicate that the capture at two times stoichiometric calcium-to-sulfur ratio was of the order of 20 percent and that, for captures approaching 50 percent, as much as seven times stoichiometric was required. There are a number of reasons quoted for this relative lack of success. The two mentioned most often are: (1) dead burning of the limestone, and (2) insufficient mixing. Dead burning is the phenomenon of heating the limestone to a temperature above which the fresh calcine, lime (CaO), recrystallizes, causing the reactivity of this lime (as influenced by the surface area) to decrease dramatically. Under these high temperature conditions the potential for capture is thus reduced, and there would be a decomposition of any calcium-sulfur complexes that may have formed before the dead burning occurred. In terms of mixing, the theory was that, since the limestone was injected with relatively cold jets into streams of hot gases rising from the combustion zone, insufficient mixing and contacting of the SO_x with the sorbent occurred. Whatever is the correct explanation, it should be noted that the success in this particular effort on a wall-fired boiler was very limited. In addition, boiler operability problems, including convective pass and preheating plugging, were observed.

The other efforts, which may relate more directly to the conditions of concern to the LIMB program, were the experiments carried out in both tangentially and arch-fired boilers. In these boilers the mixing of air and fuel is delayed and, as a result, it is theorized that the peak temperatures are lower. In addition to this, the boilers are slow mixing devices where the fuel exists in a fuel-rich zone for a significant period of time before mixing with the air. For this reason both of these systems in an uncontrolled mode give relatively low levels of NO_x compared to the wall boilers of the same vintage. For both the tangentially and arch-fired boilers, sulfur capture levels approaching 50 percent for stoichiometric ratios of calcium-to-sulfur less than two have been reported in the literature.

German Experience. Within the past few years two activities related to sorbent injection for control of SO_x have been initiated in the Federal Republic of Germany. Information related to these boilers was also considered in structuring the LIMB program. While the German work is germane to the current LIMB program, differences in fuel characteristics and boiler designs do not allow direct extrapolation to U.S. boilers.

Rheinisch-Westfalisches Electrizitatswerk (RWE), the major brown coal burning utility in the Federal Republic of Germany, has performed the most advanced German effort. The properties of brown coal are between those of peat and lignite, and the brown coal is mined by a stripping technique involving a large geographical area. The characteristics of brown coal are high moisture (up to 50 percent), ash with a highly fouling characteristic because of high alkali metal content, and relatively low sulfur. The RWE work was initiated because of concern about the possibility of sulfur emissions standards for German utilities. Under normal operation the alkali in the brown coal captures a significant percent of the sulfur; however, the composition of fuel changes in such a way that, as the fuel sulfur increases, generally the alkali decreases. Under the scenario of maximum sulfur and minimum alkali, the inherent capture would probably be insufficient to meet the anticipated German regulations. For this reason RWE looked into the possibility of incremental alkali metal addition for additional capture to meet the standard. The initial work was carried out on a small down-fired research facility where sorbent effects, fuel effects, and operating variables were examined. Based on this work, the conclusion was that the sorbents in the order of decreasing effectiveness were calcium hydroxide, calcium carbonate (limestone), and calcium oxide (precalcined lime). While the activities of the calcium carbonate and calcium hydroxide were close together, the activity of calcium oxide was considerably less. Based on the results of this testing the system was installed and tested on a 60 MW (electrical) boiler in the RWE system.

Based on the success at the 60 MW scale, RWE has installed this technique on a 300 MW brown-coal-fired power plant. As opposed to the relatively simple and quick installation used at the Fortuna Station (60 MW), the 300 MW unit required a significantly more extensive equipment investment. Included in the effort were the provision of a rail siding for supply of the limestone or calcium sorbent to be used in the system, bunkering capacity, and the possibility of additional pulverization capability. The estimated cost of this effort is about $12 million or roughly $40/kW. It should also be noted that, because of the precipitator design and the reported changes in the ash characteristics, the anticipation is that no changes in the precipitators will be required to comply with the necessary particulate removal efficiencies. Therefore, no incremental costs for upgrade of the particulate collection system are included in this number.

L&C Steinmuller GmbH, one of the major German boiler manufacturers, has explored the applicability of the distributed mixing burner concept to their boilers. Following some limited pilot-scale testing at IFRF, Steinmuller exercised a target of opportunity at a 700 MW boiler located in the Saar region of Germany. During an outage scheduled for other maintenance the burner zone of the boiler was modified to incorporate four tertiary ports in the wall around each of the existing burners. The NO_x performance of the boiler was reduced from a baseline number of around 600 ppm at 6 percent excess oxygen to around 250 ppm at 6 percent excess oxygen.

L&C Steinmuller has also done extensive pilot-scale work on sorbent injection with its staged mixing burner. Based on experimental results at 10 to 100 x 10^6 Btu/hr*, LCS has installed a sorbent injection system at the Weiher III boiler. Performance evaluation is scheduled for late 1984 to early 1985.

EPA Distributed Mixing Burner Testing. In 1979 a limited series of pilot-scale tests were carried out at the 10 x 10^6 Btu/hr scale using sorbent injection through the distributed mixing burner. This testing was carried out based on theoretical analyses suggesting that the presence of fuel-rich conditions and delayed heat release leading to lower peak temperatures might give a beneficial effect for sorbent removal of SO_x in second-generation low- NO_x burners. For this particular testing, the SO_x removal was evaluated based on gas-phase measurements of SO_2 in the flue gas, and no attempt was made to close the sulfur balance.

The testing was carried in the small watertube simulator (SWS) located at the EERC, El Toro, facility. The burner was a dual-throat distributed mixing burner that had been used for developing basic design criteria for second generation staged low-NO_x burners. For this test series, pre-pulverized sorbents were used. The sorbents were mixed with the coal, and the coal/sorbent mixture was passed through the pulverizer. This affected the pulverization of the coal and the intimate mixing of the sorbent with the coal. The sorbent used included limestone, sodium carbonate, trona (a mixture of sodium bicarbonate and sodium carbonate), calcium oxide (precalcined limestone), and several naturally occurring calcium- and sodium-containing minerals. Test results indicated that the effective additives were limestone, sodium bicarbonate, and trona. For limestone the observed removals ranged from approximately 50 percent at a calcium-to-sulfur stoichiometry of 1 to 80 percent at a calcium-to-sulfur stoichiometry of 3. For the sodium-based additives the removal ranged from 40 percent at a sodium-to-sulfur stoichiometry of 2 up to 70 percent for a sodium-to-sulfur stoichiometry of 4. While the absolute levels of emission reduction should be viewed with caution, the results gave sufficient incentive to pursue the technology further. As a result of these tests, a number of hypotheses were formulated as to the critical parameters in the reaction of limestone with sulfur in distributed mixing burners. These include:

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* 1 Btu = 1.06 kJ.

(1) Intimate mixing of the sorbent with the coal leads to a high degree of contacting of the active sorbent with the sulfur early in the flame.

(2) Contacting of the calcium and sulfur under fuel-rich conditions leads to the formation of calcium sulfide, which is stable to higher temperatures.

(3) Peak temperatures in the burner are believed to be reduced. In addition, the SWS has a relatively cold firebox. Both of these lead to lower peak temperatures and therefore a higher likelihood of retention of the sulfur by the sorbent once captured.

(4) The in-flame calcination of calcium carbonate leads to a potentially higher activity of the sorbent and an enhancement of surface area during the calcination. When this process occurs in intimate contact with the sulfur specie, the capture may be enhanced. The relatively poor results with pre-calcined limestone tended to substantiate this hypothesis.

(5) There is evidence that the limestone exiting the combustion zone has a high level of residual activity which could lead to subsequent capture of sulfur in the convective passes of the SWS.

Structure Of The Program

This background information was used in structuring the LIMB program, which was initiated by the EPA in 1981. LIMB combines sorbent injection for SO_x control with low-NO_x burners for NO_x control. Low-NO_x burners of various designs have been developed by both EPA and private industry and are capable of retrofit applications. The SO_x control by sorbent injection is an emerging technology which has been developed by the EPA. The reaction of SO_x with sorbents (i.e., limestone and other alkaline solids) is well known under proper conditions (e.g., wet FGD). LIMB is based on injection of a sorbent directly into the furnace and its subsequent reaction with gas-phase SO_2 to form a dry calcium sulfate. The amount of SO_2 that can be captured is dependent on the type and amount of sorbent, its mixing with combustion gases and fly ash in the furnace, and its thermal history. The relative simplicity of the technology lends itself to a relatively low cost retrofit on a wide variety of systems. The program has been structured to give the best probability of achieving the stated goals of moderate SO_x and NO_x control (50-60 percent) at low cost with applicability to the major portion of the existing boiler population. A secondary objective is to improve the SO_x removal efficiency to 70-90 percent for new sources, with possible retrofit in selected cases. To achieve this, work has been concentrated in four major areas, as discussed below.

Generic R&D. The program is centered around generic R&D to provide a complete understanding of the important factors in sulfur capture by sorbents. This work is performed in experimental systems which simulate conditions in a boiler without being subject to hardware constraints. The results to date have shown that the sulfur capture is strongly dependent on conditions within the boiler which determine not only the activation of the sorbent but also the resultant reaction with SO_2. This work has shown the necessity for considering sorbents other than limestone (e.g. dolomitic and calcitic hydrates). The generic R&D is currently concentrated in improved sorbent activity for retrofit systems, although it also has application to new systems.

Prototype Testing. The results of the small-scale generic R&D must be scaled up to practical systems. As an intermediate step prior to a demonstration prototype, testing is carried out in large experimental systems. In addition small boilers may be used to provide R&D data on scale-up, operability, and reliability.

Wall-fired Boilers Demonstration. Wall-fired boilers, one of the two major types of boilers, are sold by three manufacturers: Babcock and Wilcox, Foster Wheeler, and Riley Stoker. The wall-fired boiler, which is a major source of SO_2 and NO_x, has been the subject of the initial LIMB development because both the R&D background and large-scale experimental facilities were available. The demonstration program for a representative wall-fired utility boiler was initiated in FY84 and is discussed in more detail below.

Generalization of the Technology. To be widely accepted, a well defined set of criteria for application of LIMB to a wide range of boiler designs, coals, and sorbents is necessary. A limited number of demonstrations alone may not be sufficient for widespread private sector commercialization. A key element of the overall program is to produce the required information and methodologies for applying LIMB R&D to site specific design decisions for any given boiler. This will be accomplished by a combination of modelling techniques and supporting measurements on operating boilers.

RESEARCH AND DEVELOPMENT PROGRAM STATUS AND PLANS

This section discusses the current status and R&D plans for each of the four major program areas discussed in the program description above.

Generic R&D

The LIMB program has been based on the fact that a complete understanding of the process is necessary to give the maximum probability of successful commercialization by the private sector. Generic R&D is relatively independent of the hardware-specific constraints of practical boilers and provides information essential for application of LIMB to all boiler designs. This section provides a brief description of the current status, followed by a detailed discussion of plans for FY85 and following years.

Current Status. The R&D has provided an excellent insight on the effects of critical process parameters on SO_2 capture. It has shown how these parameters affect sorbent activation and subsequent sulfur capture as a function of combustion system conditions. It has also provided an understanding of fly ash/sorbent mixture characteristics as related to slagging, fouling, and particulate capture. As a result of these findings, it has been concluded that limestone alone will not achieve the LIMB sulfur capture goals for many units in the U.S. boiler population. However, it has also provided at least two alternate sorbent approaches capable of meeting or substantially exceeding the goal of 50-60 percent capture. These approaches, which are high surface area sorbents and promoters to enhance sorbent activity, are discussed below:

Major Generic R&D Areas. The continuing small-scale R&D needs are divided into three major areas:

1. Inhouse research has identified high surface area sorbents as a key factor in obtaining high sulfur capture. It has been shown that high surface area can be generated external to the combustion process and/or in situ. These materials, which are processed limestone (e.g., hydrates), have shown the potential for sulfur capture in excess of 70 percent. The planned R&D addresses methods for obtaining highly reactive sorbents, for optimizing reaction conditions to achieve maximum capture, and for minimizing sorbent costs.

2. Another key factor is the interaction of sorbents with mineral matter which can either enhance or degrade the sorbent reactivity. The most promising results indicate that it may be possible to add small amounts of relatively inexpensive, innocuous promoters (mineral compounds) which will enhance the sorbent activity. Sulfur captures approaching those of high surface area sorbents have been achieved with promoted limestone in limited bench scale experiments. It also appears that promoters can significantly improve the performance of high surface area sorbents (e.g., hydrates). A significant effort is necessary to understand the enhancement mechanisms and to provide the basis for use in practical systems. It should be noted that a similar understanding is necessary for other sorbent/mineral matter interactions which can inhibit sulfur capture and which affect slagging, fouling, and collection characteristics of the particulate.

3. Process analysis has indicated substantial benefits may be derived from recycle of unreacted sorbent and promoters. In addition, utilization of the spent sorbent and fly ash has significant potential economic benefits. Pilot scale R&D is necessary to evaluate the engineering feasibility of these process options.

Prototype Testing

Extensive prototype testing of wall-fired boiler low-NO_x burners has been conducted to evaluate sulfur capture potential with injection of conventional sorbents. A substantial data base exists for both NO_x and SO_x control potential of a number of experimental and commercial burners. Any additional work will be in support of site specific decisions for the wall-fired demonstration.

The emphasis will be shifted to tangentially fired prototype systems and to use of improved sorbents, which are identified in generic R&D, for all systems. Tangential prototype work will be initiated in a large-scale experimental facility with a firing system producing a vortex flow field typical of that boiler class. In addition, a cooperative testing R&D program will be conducted on a small boiler (20-40 MW) to evaluate sulfur capture potential, operability, and reliability over short periods with fuel and sorbent flexibility. The prototype work will concentrate on evaluation of optimum sorbents and injection methods to maximize SO_2 capture.

Wall-fired Demonstration

The contract for the wall-fired demonstration was awarded in September 1984 to Babcock & Wilcox Company. LIMB will be installed on a 105 MW single-wall-fired unit at the Edgewater station of Ohio Edison Company. The final site specific design for the installation will be completed in February 1986. Long term testing over a 1 year period will begin in July 1987, and a report documenting the performance evaluation will be completed late in 1988. The funding to complete the effort is provided in the FY85 budget, and no outyear contingency funds are identified.

Technology Generalization

For ultimate widespread use of the LIMB technology, the R&D results must be integrated with the full-scale boiler demonstration results to provide guidance for commercialization by the private sector. The program includes: 1) process analysis to evaluate applicability and economics for specific systems; and 2) process modelling to provide a methodology useful for site specific designs. The process analysis emphasizes LIMB system options for application to different boiler classes in the population and for minimizing the cost per unit SO_2 removal. The process modelling will provide component models for thermal history, sorbent activation and reaction, injection, and mixing.

SUMMARY

The LIMB R&D program has provided a detailed understanding of the key processes governing sulfur capture with sorbents. While it appears that limestone alone will not achieve program goals, several other promising sorbents have been identified. Based on the R&D results and cost estimates of the use of these sorbents, LIMB shows substantial promise as a SO_x and NO_x control technology for retrofit applications. The ongoing R&D program should resolve the remaining technical questions and provide a basis for wide-spread private sector commercialization.

This paper provides a brief history of sorbent injection technology, synopsizes the status of LIMB R&D, and discusses future program plans.

OVERVIEW OF CANADIAN RESEARCH, DEVELOPMENT AND DEMONSTRATION PROGRAM FOR LOW NO_x/SO_2 CONTROL TECHNOLOGIES

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ABSTRACT

One of the major concerns, associated with the expanded use of coal for heat and electricity, is the emission to atmosphere of the acid rain precursors, NO_x and SO_2.

This paper outlines the technologies, the status of research, development and demonstration activities and future plans for Low NO_x/SO_2 control technologies in Canada. It includes federal government activities as well as those of the Canadian Electrical Association.

INTRODUCTION

In Canada we receive some criticism that because we have no flue gas scrubbers on our utility industry we are doing little or nothing about acid rain as one of the major concerns associated with the expanded use of coal for heat and electricity. I therefore welcome this opportunity to present to you our Canadian strategy and program for control of the acid rain precursors, NO_x and SO_2 emissions to the atmosphere. In 1982, North American utility boilers emitted over 6.8 million tonnes of NO_x and 15.8 million tonnes of SO_2 with Canadian utility sources accounting for about 3.5% of the NO_x and 5.3% of the SO_2 emissions. Of the total SO_2 emissions in Canada 60% is smelter originated and 15% from utility sources.

STRATEGY

Our strategy for utilities is based on the concept of cost effective control of acid gas emissions from fossil-fuel-fired thermal generation with the realization that direct involvement by the utility industry is essential for the success of our program.

Energy, Mines and Resources Canada embarked on two paths: one to develop control technologies for existing sources and the other for new sources.

Control technologies for existing sources includes coal beneficiation, coal/water mixtures, absorbent injection in low NO_x designed burners and advanced slagging combustors. New source technologies centre on fluidized bed combustion with a preference for circulating fluid bed in the utility application.

FUNDING

The federal source of funding for development and demonstration of these new technologies is mainly from the Coal Utilization Program, administered by the Coal Division of Energy, Mines & Resources (EMR). It was created in October 1980 to provide $150 million until March 31, 1986 and directed mainly to getting Maritime utilities off oil. Other sources of funds come from base annual reserves such as Canada Centre for Mineral and Energy Technology (CANMET) and the Office of Energy Research and Development (OERD). CANMET through its Energy Research Laboratories such as the Combustion and Carbonization Research Laboratory (CCRL) provide the Coal Division with technical support in their various projects.

Approximately one-third of the Canadian Electrical Association (CEA) research funds is provided by EMR who have representation on the various research committees.

PROGRAM

The federal program to reduce NO_x and SO_2 is as follows:

Project	Objective	Federal Funding
Maritime Coal Beneficiation	To assess and develop the beneficiation potential of both New Brunswick and Nova Scotia coals.	$2.1 million over 3 years.
Coal Water Mixtures	To develop a liquid coal fuel that will replace oil as a fuel in utility boilers.	Currently $7.2 million with another $8.0 million budgeted for the next 2 years.
Low NO_x/SO_2 Burner Demonstration at CFB Gagetown	To demonstrate low NO_x/SO_2 burner technology at an industrial scale.	$1.5 million
International Energy Agency - Agreement in NO_x and SO_2	Canada, Denmark and Sweden agreed to validate various non-US coals for NO_x and SO_2 emissions utilizing the advanced low NO_x burner concept.	$0.3 million

TransAlta Utilities Low NO_x/SO_2 Pilot Scale Development	To evaluate the Rockwell process and its applicability to Western and Eastern Canadian coals.	$0.3 million
Atmospheric Bubbling Fluidized Bed Technology Demonstration Canadian Forces Base Summerside and materials testing at Point Tupper Pilot plant.	To demonstrate atmospheric bubbling fluidized bed technology at the industrial scale.	Summerside - $18.0 million Point Tupper - $8.0 million
Coal/Oil Shale Circulating Fluidized Bed Technology Demonstration, Chatham, New Brunswick.	To demonstrate the circulating fluidized bed technology at 22 MW_e utilizing high sulphur coal and Oil Shale as sorbent.	$36.0 million
EMR/CANMET Fluidized-Bed Research and Development.	To evaluate NO_x and SO_2 suppression in bubbling and circulating fluidized-bed with Canadian coals and sorbents.	$2.0 million
	Total Federal Funding:	$83.4 million

STATUS OF PROJECTS

Coal beneficiation, coal/water mixtures and the Point Tupper materials testing project being peripheral to the theme of this symposium will not be reported in this paper.

Canadian Forces Base Gagetown Demonstration

As part of an on-going effort to expand the use of high-sulphur Maritime coal for heat and electricity with minimal environmental impact, CANMET has initiated a project to demonstrate limestone injection, multi-stage burner technology (LIMB) for substantially reducing acid gas emissions from pulverized-coal-fired boilers. The project, which is being carried out with the active participation of the Department of National Defence and the analytical support of Environment Canada, involves the retrofitting of an existing 20 MW hot water generator at CFB Gagetown with two "staged-mixing" burners. These are designed to inhibit the formation of nitrogen oxides by flame modification and to suppress the emissions of sulphur oxides by limestone injection with no reduction in boiler efficiency.

Each burner is rated at 10 MW_{th} and is designed to achieve a 50% reduction in NO_x and SO_2 emissions while burning a 3% sulphur eastern Canadian coal. The installation of equipment on Unit No.2 at CFB Gagetown was completed in April 1984 and burner shakedown trials under the supervision of the contractor (Volcano Inc.) are in progress.

Final acceptance tests are scheduled for December 1984 when weather conditions will permit full load operation of the hot water generator.

The Gagetown project, which is the first full-scale demonstration of this new burner concept to North America will provide potential users as well as research and regulatory agencies with advance information on the operational benefits of this new technology.

TransAlta Utilities Low NO_x/SO_2 Pilot-Scale Development Program

The program was initiated on December 16, 1982 when Rockwell and the first of several utilities signed Participation Agreements. Current participants are Houston Lighting and Power Company, Niagara Mohawk Power Corporation, Southern California Edison Company, TransAlta Utilities and Wisconsin Public Service Corporation. The Canadian Electrical Association participates through TransAlta.

The program, developed by Rockwell International, utilizes advanced combustion concepts for both retrofit and new installations in an attempt to reduce SO_2 emissions by up to 70% and to suppress NO_x emissions to less than 100 ppm.

Pilot plant testing at both the 4.7 MW and 7.3 MW scale have confirmed the design concept for the Rockwell burner and further work to verify specific technology features is in progress. Preliminary design work for the commercial scale 30 MWth demonstration burner has been initiated.

The demonstration program will be a three year, two-phased program which is planned for Unit No. 1 (66 MW_e) at TransAlta Utilities Corporation's Wabamun Generating Plant.

In the first phase, the 30 MWth burner complete with slag separator will be designed, fabricated, installed and tested over a 6 month period. Two additional burners will be subsequently installed, without slag separators, and intensive testing of the composite Rockwell Low NO_x/SO_2 combustion system will follow for a period of about one year.

A phased approach is used to permit the demonstration testing and shakedown so that any required modifications can be incorporated into the second and third units. Total cost of the project is approximately $10 million Canadian.

International Energy Agency (IEA) Project for Control of Nitrogen Oxides Emission During Coal Combustion

CANMET, on behalf of Canada, participates in a major project sponsored by the International Energy Agency. The project, co-funded by Canada, Denmark and Sweden with US EPA guidance and support, involves the validation and optimization of advanced burner concepts under a three-stage agreement. The work is being performed by the Energy and Environmental Research Corporation at Santa Ana, California.

Stage I, completed in March 1982, consisted of bench-scale furnace trials on 45 coals including 9 from Canada, to elucidate the mechanisms of NO_x formation from fuel nitrogen under pre-mixed and staged combustion conditions. It was determined that much of the fuel nitrogen in the volatile matter can be transformed to N_2 instead of NO. The conversion of fuel nitrogen to NO was 30% to 40% in conventional flames but only 7% to 14% in staged flames. Nitrogen retained in the char showed about 20% conversion to NO and appeared to be relatively independent of local oxygen concentration. Reductions in sulphur emissions of 50% by sorbent injection into tertiary combustion air were achievable with Ca/S ratios of 2/1.

Stage II, now in progress, consists of combustion trials in three progressively larger furnaces (50, 90 and 100 x 10^6 Btu's) to generate data for extrapolation to full-scale burner designs. Four coals, two from Canada, are being evaluated for NO_x production and two of the four coals, including one from Canada, have been evaluated for simultaneous reductions of SO_2 and NO_x using limestone sorbents.

You will be hearing about this work later on from Energy and Environmental Research Corporation, so I will not go into further details.

Chatham Coal/Oil Shale Demonstration

The New Brunswick Electric Power Commission has dedicated its Chatham generating station consisting of one 12 MW_e B&W boiler and one 22 MW_e CE boiler to research in advanced burner concepts and circulating fluidized bed technologies until March 1988 under an agreement with the Coal Division of Energy, Mines and Resources.

A pilot-scale combustion rig with a staged combustion burner ($1x10^6$ Btu/hr.) modelled on the IEA work done through EPA at Energy and Environmental Research, California is being erected at the Chatham station to study the potential of achieving acceptable acid gas emissions by co-firing coal with local oil shale. A comparison will be done with firing coal and limestone. A successful demonstration with oil shale as a sorbent could lead to further demonstration on the 12 MW_e boiler at Chatham or the 20 MW_{th} boiler at CFB Gagetown.

A 22 MW_e circulating fluidized boiler to be manufactured by CE Canada-Lurgi will be installed at Chatham to tie into the existing turbine. It is expected to be commissioned in the fall of 1986. Initially it will fire high sulphur (8%) New Brunswick coal and limestone to establish a baseline for comparison with the same coal and oil shale. The oil shale has approximately 2100 BTU's/lb. and an ash analysis of CaO 14.9% and MgO 5.5% present in the original mineral matter as a carbonate.

Canadian Forces Base Summerside AFB Demonstration

EMR in collaboration with Defense Canada is demonstrating atmospheric bubbling fluidized bed combustion at CFB Summerside, PEI, heating plant. Construction of the equipment, which consists of two Foster-Wheeler boilers rated at 18 tph of steam each, together with all ancilliaries, was completed in 1982. In the following 1-1/2 heating season commissioning trials have been underway, some modifications have been made, and the boilers have each accumulated well over 1,000 hours of operating time.

The boilers have been tested with three different Cape Breton coals ranging from 4 to 6% sulphur, and have met guarantees of capacity, efficiency and emission control with all of them.

Further demonstration tests during the 1984/85 and 1985/86 heating seasons will include co-firing of wood chips and coal, and evaluation of load response characteristics. It is also hoped to evaluate the effects of limestone size consist on sulphur capture, and to conduct combustion tests with a high ash fuel, possibly coal washery rejects. Under the contract the wastes are being characterized and specific uses in PEI are being identified.

CANADIAN ELECTRICAL ASSOCIATION (CEA) SUPPORTED ACTIVITIES

Ontario Hydro, a major utility in North America, has for several years been examining methods to reduce NO_x emission levels from its Nanticoke Generating Station. This generating station comprises 8x500 MW_e natural circulating boilers of Babcock and Wilcox manufacture, each with 40 opposed wall firing conventional circular coal burners.

In 1980, with the financial assistance of the Canadian Electrical Association Ontario Hydro employed the services of B&W (Canada) to undertake detailed design, manufacture, and installation of modifications to eight burners (one row). Subsequent testing proved that these modified burners performed satisfactorily and reduced NO_x emissions by 20% below the unmodified burner emissions.

Based on this moderate success, Ontario Hydro in 1983 converted all of number 5 and 6 units at Nanticoke. This resulted in a high carbon carryover in the ash. As a result of the high carbon, Ontario Hydro had B&W do some modelling at their Alliance laboratories looking at possibly 40% NO_x reduction with less than 6% carbon carryover. Modified burner changes based on the modelling is planned for October 1984.

Ontario Hydro is also considering converting some burners on their corner-fired units at Lakeview to the C-E Low NO_x Concentric Firing System and experimenting with finely powdered limestone injection.

TransAlta Utilities, Calgary, Alberta as a member of the consortium interested in developing the Rockwell burner received the support of the Canadian Electrical Association Generation R&D Committee. To enable them to have a more prominent position in the development process, the Alberta/Canada Energy Resources Research Fund is supporting, pending successful pilot scale trials at Rockwell's California facility, the demonstration of a 30 MWth burner at TransAlta's Wabamun generating station.

The CEA Generation R&D Committee also supported the installation of the Combustion Engineering Low No_x Concentric Firing System at Saskatchewan Power Corporation's Boundary Dam Generating Station 300 MW lignite fired Unit #6. Dave Winship, CE Canada, will be giving a report on the results later on in the symposium.

CONCLUSIONS

So you see, Canada is not only concerned about acid gas emissions, but is doing something about it. Canadian utility's contribution of SO_2 to acid rain is only 5.3% of the total for North American utilities, but our efforts to control this environmental problem is a major priority. Our RD&D activities address both short-term regional concerns as well as the longer term issues associated with the expanded use of coal.

THE UTILITY PERSPECTIVE ON DRY SO_2 CONTROL TECHNOLOGIES

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ABSTRACT

This paper summarizes current understanding and provides comparative descriptions of two promising techniques for dry SO_2 control in utility applications: flue gas sodium sorbent injection, and in-furnace calcium sorbent injection. In both cases, dry sorbents are injected in powdered form and react chemically with SO_2 to form a dry particulate waste which potentially can be collected in either a baghouse or electrostatic precipitator (ESP). Two electric utilities, Public Service Co. of Colorado and the Colorado Springs Dept. of Public Utilities, have announced firm plans to employ flue gas sodium sorbent technology. In-furnace calcium sorbent injection is still under active development and no long term utility commitment to this technology has yet been made in the United States. Both control techniques show potential as reliable, efficient, and economic SO_2 control options, giving utilities greater flexibility in meeting their environmental control responsibilities.

INTRODUCTION

This paper summarizes current understanding and provides comparative descriptions of two promising techniques for dry SO_2 control in utility applications: flue gas sodium sorbent injection, and in-furnace calcium sorbent injection. In both cases, dry sorbents are injected in powdered form and react chemically with SO_2 to form a dry particulate waste. With sodium sorbent injection, the waste sodium material is collected along with particulate fly ash in a fabric filter dust collector (baghouse). With calcium sorbent injection, the calcium waste material is collected in either a baghouse or electrostatic precipitator (ESP). Figure 1 is a schematic of a coal-fired power plant showing, for both types of sorbents, their injection, SO_2 capture, and solid waste removal sites. This paper discusses the advantages and disadvantages of these two control technologies and the implications and prospects for utility application.

Sulfur-dioxide emission control is presently required for all new coal-fired power plants. The EPA New Source Performance Standards stipulate 70% SO_2 removal for plants burning low-sulfur coal, and 90% removal for those burning high-sulfur coal. In both cases, emissions may not exceed 1.2 lb per million Btu of heat input to the boiler.

Conventional wet scrubbing is an effective option in meeting these standards. However, wet scrubbers are costly -- accounting for as much as 25% of the capital and operating costs of a new 1000 MW plant -- and are often problematic to operate, requiring complex hardware and the use of substantial quantities of water. Costly liquid waste treatment systems are required and result in additional complexities and expense.

Spray drying, the second generation in SO_2 control technology, may be a lower capital cost alternative to wet scrubbing. While this technology has eliminated the need for liquid waste treatment systems, it is still necessary to prepare a wet slurry for injection.

Dry sorbent injection control techniques simplify the sulfur dioxide removal process by eliminating the wet slurry, liquid waste treatment system, and extensive additional hardware, thus resulting in lower comparative capital costs. Also, these systems use equipment already familiar to power plant operators. Operating costs can be significant, depending largely on reagent cost, but overall system cost in virtually any imaginable scenario will be considerably less than that for wet scrubbers. This is the case because with dry control techniques sorbent cost and utilization efficiency have the greatest impact on total system costs -- not system hardware, as with wet scrubbers and spray dryers. Further, dry sorbent reagent costs are expected to decrease as suppliers expand their efforts to make new, more efficient products available at lower prices. Other advantages of dry sorbent injection systems include:

- System simplicity contributes to improved reliability.
- Power costs are lower.
- Scaling and corrosion are minimal.
- Flue gas reheating is not necessary.
- Systems can be retrofitted to boilers with baghouses and ESPs.
- There is combined particulate and SO_2 collection.

Public Service Co. of Colorado (PSCC) has recently committed to all-dry flue gas sodium sorbent injection on a new 500 MW coal-fired boiler, Pawnee Unit 2. Although no firm date has been announced for construction of Pawnee 2, for engineering and planning purposes it is scheduled to begin service in 1990 burning western, low-sulfur subbituminous coal. PSCC's confidence in flue gas sodium sorbent injection stems from extensive testing, both bench-scale and in the field, most specifically in two years of testing at PSCC's 22 MW Cameo Station Unit 1. PSCC and the Colorado Springs Dept. of Public Utilities are currently the only electric utilities to announce firm plans to employ flue gas sodium sorbent injection.

In-furnace calcium sorbent injection is still under active development and no long term utility commitment to this technology has yet occurred in the United States. Laboratory test results and recent large-scale exploratory tests indicate the high potential of this process as a low-cost option for SO_2 control. Continued development and large-scale demonstrations planned over the next few years are expected to confirm the SO_2 removal potential and resolve remaining cost and plant impact issues.

Figures 2 and 3 illustrate the variety of options available to utilities in the selection of particulate and SO_2 control technologies, and reflect the complexity of the decision-making process in this area.

FLUE GAS SODIUM SORBENT INJECTION

The three sodium sorbents which have received most utility and supplier attention to date are nahcolite (naturally occurring sodium bicarbonate, $NaHCO_3$), trona (naturally occurring $NaHCO_3 \cdot Na_2CO_3 \cdot 2\ H_2O$), and sodium sesquicarbonate (a trona analogue, $NaHCO_3 \cdot Na_2CO_3 \cdot 2\ H_2O$).

In the dry-injection process, the sodium sorbent is pulverized and fed into the flue gas stream (nominally at a temperature of 300°F) ahead of a baghouse and downstream of the air heater. In the ductwork, the sodium bicarbonate in the sorbent particles decomposes to sodium carbonate (Na_2CO_3) in a "popcorn" fashion, forming an open, porous microstructure exposing more particle surface area. As shown in Figure 4, the sorbent reacts with the SO_2 in the flue gas, forming sodium sulfate, and subsequently is collected along with the fly ash as part of the dustcake in the baghouse. Contacting of sorbent and SO_2 on the dustcake results in further SO_2 removal. Typically, 20-30% of the SO_2 collection occurs in the ductwork, and the remaining 70-80% in the baghouse.

Historical Perspective and Process Development

It has been known for some time that sodium reagents chemically react with SO_2 to form sodium sulfate and sodium sulfite. Until recently, however, this reaction was not seriously considered for SO_2 control in coal-fired power plants because it was thought there was no practical way to bring the two chemicals into contact long enough to react, and then to collect the by-products. However, the emergence of the baghouse in the utility industry resolved this issue by providing both efficient particulate collection and allowing for an extended period of SO_2-sorbent contact.

Identification of an appropriate sodium-based reagent has also been an issue in development of this technology. Initial reagent testing was conducted with nahcolite, the preferred alternative because of its high sodium bicarbonate content and higher SO_2 collection efficiencies -- in excess of 70% removal. Over 30 billion tons of nahcolite have been identified in the western United States. However, the resource is locked in oil shale formations, and the recent slackening of interest in oil shale has made its future availability uncertain. While long-range prospects for mining nahcolite are unclear, efforts are under way to produce nahcolite through solution mining techniques.

In contrast, trona is commercially available in large quantities, and recent tests have shown that it too can achieve 70% SO_2 removal. In excess of 85 billion tons of trona are estimated to exist in the western United States, and the material is now being mined as a source of soda ash (Na_2CO_3) for glass-making by a number of companies. Trona availability for SO_2 collection has been enhanced by the recent downturn in its demand by glass manufacturers due to the decline in new building construction and the use of less expensive glassware substitutes. In addition, trona suppliers are now undertaking research and development programs of their own to improve the mineral's SO_2 collection characteristics for utility application. These investigations are focusing on both sodium sesquicarbonate and other proprietary compounds.

The first utility testing of flue gas sodium sorbent injection used nahcolite as the reagent and was conducted in the mid-1960s by Southern California Edison Co. at its Alamitos station on an oil-fired boiler equipped with a baghouse. Although SO_2 removal was not quantified, results were said to be encouraging(1,2). Subsequent tests in the late 1960s and early 1970s by Wheelabrator-Frye in conjunction with the Public Service Co. of Indiana and, separately, with Colorado-Ute Electric Association, by the Air Preheater Co. with Public Service Electric and Gas Co. of

New Jersey (under contract with the National Air Pollution Control Administration), and by Superior Oil Co., with PSCC at its Cherokee Station, showed that a variety of sodium based reagents -- including nahcolite, sodium carbonate, and commercial and predecomposed sodium bicarbonate -- could achieve SO_2 removal rates in the range of 70-90%(2,3,4,5). It is important to note, however, that sodium carbonate, or soda ash, has proven to be largely ineffective as an SO_2 adsorbent.

In the late 1970s, the Electric Power Research Institute (EPRI) sponsored a bench-scale experimental investigation of sodium sorbent injection specifically to quantify SO_2 removal with low-sulfur coals(6). This testing, conducted by KVB, Inc., demonstrated for the first time that trona could achieve SO_2 removal efficiencies comparable to -- although not as high as -- nahcolite. Additionally, these tests showed the effectiveness of the sodium compounds to be greatly dependent on the quantity of sorbent injected relative to SO_2 concentration in the flue gas, a measure quantified in terms of normalized stoichiometric ratio (NSR).* For example, to achieve 70% SO_2 removal using nahcolite, a NSR of 1.1 was required. To achieve the same level of collection with trona, a NSR of 3.0 was required. Temperature was also found to affect removal efficiency. Injecting nahcolite in a higher temperature zone (approx. 500°F) will increase SO_2 removal efficiency a small percentage, whereas with trona, the higher temperature injection decreased SO_2 removal efficiency.

In 1981, EPRI, PSCC, Stearns-Catalytic, and Multi-Mineral Corp. jointly embarked on a field evaluation of flue gas sodium sorbent injection at the Cameo Station(7). As shown in Figure 5, five sodium compounds were analyzed with results showing 70% SO_2 removal for nahcolite and trona at NSRs of 0.75 and 1.3, respectively.

Economics

The overall simplicity of the dry sodium injection system results in capital costs significantly lower than those of conventional wet scrubber systems. Preliminary economic analyses have indicated a capital cost advantage of $100-150/kW compared with conventional wet scrubbing for new or retrofit boilers, depending on site-specific factors.

To further assess the economics of flue gas sodium sorbent injection, EPRI recently sponsored a study conducted by Stearns-Catalytic(8). This work compared the costs of commercially sized nahcolite and trona all-dry injection systems with commercially available spray dryer systems. The analysis was performed for a new, hypothetical power plant located in Kenosha, Wisconsin, consisting of two 500 MW units burning a western, low-sulfur (0.5%) coal, and assumed a 30-year plant life. Capital costs of trona and nahcolite dry-injection systems were about $25/kW, compared to $115/kW for spray drying. On a levelized cost basis, trona injection was least expensive, followed by nahcolite injection and spray drying. These results were found to be highly sensitive to the delivered price of the sorbent, sulfur content of the coal, and SO_2 removal requirement. Cost for waste disposal and the size of the generating plant were found to be important, but less significant. Since this economic analysis was for a hypothetical power plant site, it does not take into account site-specific considerations. Consequently, any electric utility considering the technology is encouraged to conduct an analysis of its own for each plant site.

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*NSR is defined as: $\frac{1/2 \text{ moles of Na}}{\text{moles of S}}$
which gives a value of 1.0 when two moles of Na react with one mole of S to produce one mole of Na_2SO_4 product.

PSCC has performed an economic analysis for Pawnee Unit 2, comparing costs for spray dryer and dry injection systems. The study assumed startup of Pawnee in 1990, a 30-year plant life, and the consumption of 70,000 tons/year of sorbent. Costs included the particulate control system for both spray dryer and dry-injection systems, as well as costs for the balance-of-plant systems required with either SO_2 removal technology, and were found to be unquestionably size-, site-, and schedule-specific(2). Costs were calculated assuming the use of trona as the dry sorbent; costs for nahcolite would be expected to be less due to a lower reagent requirement. The total capital investment for the dry-sorbent system was $57 million, substantially less than the $120 million estimated capital investment for the spray dryer system at this site. The dry-sorbent system is expected to have higher annual O&M costs, however, mainly due to the larger quantities of reagent needed to accomplish the same SO_2 removal. In spite of this projected higher cost for reagent, the dry injection system has an $8 million lower annual evaluated cost, which includes the annualized capital cost plus the annualized O&M cost.

Issues In Utility Application

Although flue gas injection of trona has proven to be the economic choice for SO_2 control at Pawnee, a number of issues are appropriate for more detailed discussion and analysis by other utilities considering the technology.

Waste Disposal. Sodium salts produced by the reaction of SO_2 with sodium-based dry sorbents are very soluble in water. Although the weight fraction of sodium in the waste product -- which also includes fly ash -- is less than 10%, precautions must be taken to avoid leaching of sodium into ground or surface waters. Clay-lined holding ponds preclude leaching and can be utilized to address this concern. Alternatively, a technique to fix sodium ions in the residue, rendering it insoluble, is currently under development. Such a process could potentially permit disposal of fly ash, spent sorbent, and bottom ash together in a conventional landfill. In a plant originally constructed with an ESP, a baghouse and dry injection system could be added for SO_2 control. Under this approach, the ESP collects the major portion of the fly ash while the baghouse collects all of the spent sorbent and the remainder of the fly ash. The spent sodium/fly ash mixture is then disposed of separately from the fly ash, thus allowing fly ash to be utilized as a concrete additive and return of the spent sodium to its origin.

Use With High-Sulfur Coal. To date, dry sorbent injection has been demonstrated only on coals with sulfur contents below 0.8%. However, recent work by sorbent suppliers indicates that the upper limit may reach as high as 2-3%. Even if sufficiently high SO_2 collection efficiencies could be obtained on high-sulfur coals -- standards as high as 90% may be required -- this would necessitate the use of very large amounts of sodium reagent and potentially increase reagent costs to the point where the process would no longer be economic.

Use With ESPs. Most research to date has been conducted using baghouses for particulate collection. Preheating sorbents prior to injection in system ductwork is a concept now being explored to facilitate the use of this technique with ESPs. The objective is to increase reactivity of the sorbent such that SO_2 collection efficiencies in the ductwork alone are acceptable. In-duct SO_2 collection of 20-30% has already been demonstrated, and 50% appears possible.

Policy Issues. The question of whether flue gas sodium sorbent injection can and will qualify as best available control technology (BACT) as defined by the EPA is another potentially important issue in considering the technology. Preliminary discussion with regulatory agencies, combined with the obvious simplicity and low cost of the process, have resulted in favorable reaction.

IN-FURNACE CALCIUM SORBENT INJECTION

With in-furnace sorbent injection, a pulverized calcium-based material such as limestone ($CaCO_3$) or calcium hydroxide (hydrated lime $Ca(OH)_2$) is injected directly into the furnace cavity of a coal-fired boiler. As shown in Figure 6, the sorbent rapidly decomposes (a limestone sorbent, for example, releasing CO_2; hydrated lime releasing H_2O), to form a porous microstructure with greater exposed surface area. The resulting lime particles are highly reactive and chemically combine in suspension with SO_2 to form solid calcium sulfate ($CaSO_4$). This calcium sulfate, along with any unreacted lime, is then collected with fly ash in a baghouse or ESP. In essence, this process attempts to apply to pulverized coal-fired boilers an SO_2 control technique similar in overall chemistry to that used in fluidized bed boilers -- albeit under distinctly different temperature, residence time, and combustion conditions.

Historical Perspective and Process Development

The concept of furnace sorbent injection originated in the early 1960s. It was felt at the time that direct injection of limestone followed, for example, by wet particulate scrubbing was the least complicated and most economic procedure for meeting anticipated SO_2 and particulate removal requirements. However, trial tests in laboratory furnaces and full-scale utility boilers in the United States, Europe, and Japan generally failed to demonstrate sufficient SO_2 removal at practical sorbent-to-sulfur ratios. SO_2 removal during tests at utility boilers typically ranged from 15-40%, well below the target values of 80-90%. Removal efficiency was also found to be highly dependent on boiler design and operation, as well as on the type of sorbent and injection system used. Potential adverse effects on boiler performance, principally increased slagging and fouling of boiler heat transfer surfaces and degraded ESP performance, were also noted. Given these concerns and the lower-than-anticipated SO_2 removals, testing was essentially abandoned by the early 1970s(10).

Interest in the technology was rekindled in the mid-1970s with research performed in West Germany. This work arose out of a need to develop practical methods for incremental SO_2 removal in West German plants burning lignite coal. The experiments showed better results than any previous tests and triggered a multi-year development program in that country, including testing of bituminous coals. In the United States, the EPA announcement of the LIMB concept in the late 1970s was a major factor in accelerating interest in this country.

Another factor now contributing to the resurgence of interest in in-furnace dry sorbent injection is the growing incentive for developing low-cost incremental SO_2 controls applicable to both existing and new power plants. The potential also exists for combining in-furnace sorbent injection with other SO_2 control technologies. For instance, use in conjunction with coal cleaning or coal blending may provide flexibility in achieving SO_2 emission compliance or allow the purchase of less expensive, higher-sulfur coals for existing units. Also, integration of the process with other flue gas treatment systems may provide an overall SO_2 control capability adequate to meet higher requirements for new plants.

Recent experimental work in the United States and Europe indicates the possibility of achieving high SO_2 removal efficiencies at practical sorbent injection rates if sorbent characteristics and injection conditions are properly controlled.

Figure 7 shows percentage SO_2 removals for pressure hydrated lime, calcium hydroxide, and limestone at various Ca/S molar ratios based on pilot laboratory tests jointly sponsored by EPRI and Southern Company Services. These tests and supporting bench-scale experiments, engineering studies, and information exchanges will set the groundwork for utility tests of in-furnace sorbent injection in the 40 to 100 MW range. Demonstrations of this scale are planned as a necessary intermediate step in the development process prior to application at full-size utility boilers.

Parallel R&D programs are under way at EPA, DOE, and several other utility, industrial, and manufacturing organizations, as well as in other countries, including Canada, West Germany, France, The Netherlands, Austria, and Japan. These various programs span a wide range of laboratory and field test conditions and involve a variety of sorbents, coals, and injection system designs. Sorbent suppliers are also involved. As a result, within the next two years a tremendous amount of new information on process chemistry, SO_2 removal performance, and system design will be made available.

Economics

Since this process uses existing furnace cavities and particulate control devices for SO_2 reactions and removal, capital costs are expected to be much lower than those associated with wet scrubbers. However, the developmental status of the technology and uncertainties about final process design and plant impact issues makes it difficult to accurately estimate costs. Preliminary estimates range between approximately $30 and $80/kW for retrofits. Costs for new unit applications may be at the lower end of this range.

Operating costs for these systems depend strongly on sorbent utilization and coal sulfur content. Calcium-based materials are readily available at low cost. However, current utilization efficiency, which to date has been 20-30% for limestone and up to 40% for lime, is less than for sodium sorbents, thereby increasing costs for sorbent supply and solid waste handling and disposal. Current efforts to improve calcium utilization, if effective, could reduce in-furnace injection operating costs appreciably.

Issues in Utility Application

A number of issues remain to be resolved before in-furnace calcium sorbent injection can be considered a practical control option for full-scale utility application. Most of these issues are of a technical nature and, although none appear insurmountable, the costs involved in solving them are as yet unknown.

Impact on ESPs. In-furnace calcium sorbent injection can double or triple solids loading to the boiler, depending on coal sulfur content, sorbent type, and Ca/S ratio. Greater solids loading, in turn, increases ESP particle inlet loading, while the calcium compounds increase resistivity in the ESP. These factors together can degrade ESP performance and can result in higher particulate emissions, especially for marginally performing units. Efforts are now underway by vendors and others to quantify the problem and verify retrofit upgrading techniques, such as chemical and thermal flue gas conditioning. There is no evidence at this time that in-furnace sorbent injection adversely affects fabric filter baghouse operation.

Ash Handling and Disposal. In-furnace calcium sorbent injection produces solid wastes greatly different from conventional ash. Unreacted sorbent, fly ash, and reaction by-products have different disposal characteristics and requirements which must be better understood. Specifically, the possible need for special handling, transport, pretreatment, and disposal of the by-products must be clarified before the technology can be widely employed.

Boiler Slagging and Fouling. Increased solids loading to the boiler can change the chemical and physical properties of the ash, thereby raising concerns about increased slagging and fouling on furnace heat transfer surfaces. Research to date indicates that these deposits likely can be managed with conventional sootblowing equipment. However, additional sootblowers and/or more frequent use may be required(11). Field test activities planned and currently in progress will provide further insight into these issues.

System Design. While in-furnace calcium sorbent injection appears to be a feasible means to control SO_2 emissions, much work remains to be done to optimize the process. This includes determination of optimum injection system design, the most efficient type of sorbent(s), and of a means for enhancing sorbent utilization.

Recent studies have identified the upper furnace cavity as the best site for calcium sorbent injection(11,12). Injection in this post-flame area effectively decouples the process from the combustion system, thereby facilitating retrofit and significantly expanding the number of boilers in which the technology could be applied.

With regard to sorbent-SO_2 capture efficiency and enhancement, most R&D to date has focused on evaluating commercial dolomitic and high calcium limestone and lime sorbent materials. The efficiency or reactivity of these compounds has been evaluated under a variety of test conditions and furnace designs. Results suggest that the size and surface area of the calcined sorbent play a major role in SO_2 capture efficiency. There are also indications that chemical constituents and physical micro-structure of the sorbent are important. Some of these factors are strongly influenced by the thermal history of the sorbent in the furnace. Future work will focus on understanding the role of these various factors, how they are influenced by the thermal or chemical environments that the sorbent is exposed to and, ultimately, how these environments can be created or manipulated to enhance sorbent characteristics for optimum SO_2 capture.

Policy Issues. The question of whether in-furnace calcium sorbent injection can and will qualify for BACT status is another potentially important issue in considering the technology.

CONCLUSION

Evolution of SO_2 control technologies for utilities from the wet scrubber to the spray dryer and dry injection processes shows a progressive development towards simpler, more economic systems. Planned installation of a flue gas sodium injection system at PSCC's Pawnee Station will represent a major step in development of that technology. Additionally, demonstrated increased interest on the part of suppliers in providing new, improved sodium sorbents to the utility market is encouraging. As regards in-furnace calcium injection, laboratory results to date are optimistic for development of a commercially viable system, and field demonstrations scheduled to be underway in the next few years will represent a major milestone towards commercialization.

Emergence of these technologies as reliable, efficient, and economic SO_2 control options gives utilities greater flexibility in meeting their environmental control responsibilities, and presents a real opportunity for reducing the cost of electricity to their customers.

ACKNOWLEDGMENTS

The author wishes to thank the Coal Combustion Systems Division of the Electric Power Research Institute for its assistance in the preparation of this paper. Also, Eduardo E. Gonzales, Professional Engineer, and Robert D. Gates, Supervisor, Mechanical Engineering, of the Public Service Co. of Colorado provided important background and data on PSCC's evaluation of flue gas sodium sorbent injection for Pawnee Unit 2.

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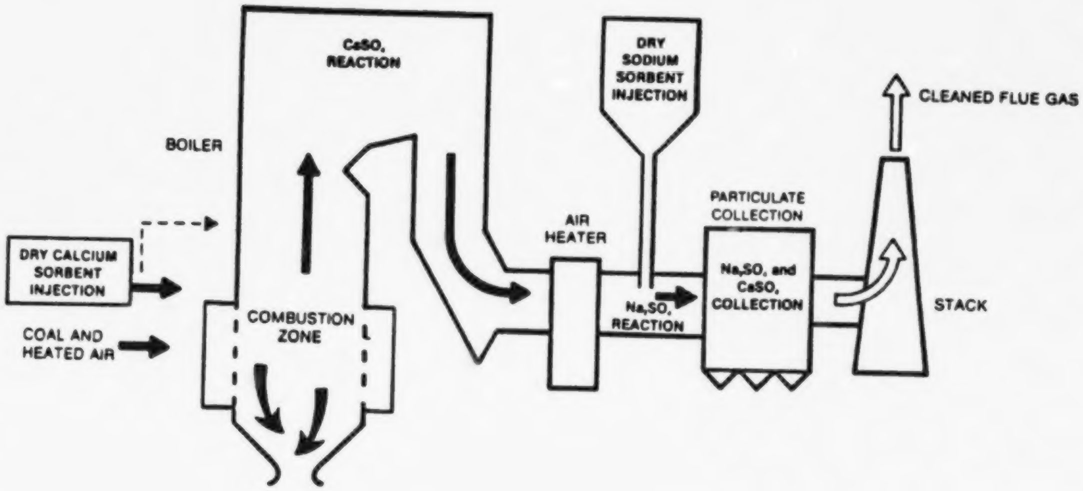

$CaSO_4$ REACTION
DRY SODIUM SORBENT INJECTION
CLEANED FLUE GAS
BOILER
PARTICULATE COLLECTION
AIR HEATER
DRY CALCIUM SORBENT INJECTION
Na_2SO_4 and $CaSO_4$ COLLECTION
COMBUSTION ZONE
Na_2SO_4 REACTION
STACK
COAL AND HEATED AIR

Figure 1. Schematic of a coal-fired power plant, showing sodium and calcium sorbent injection and removal sites.

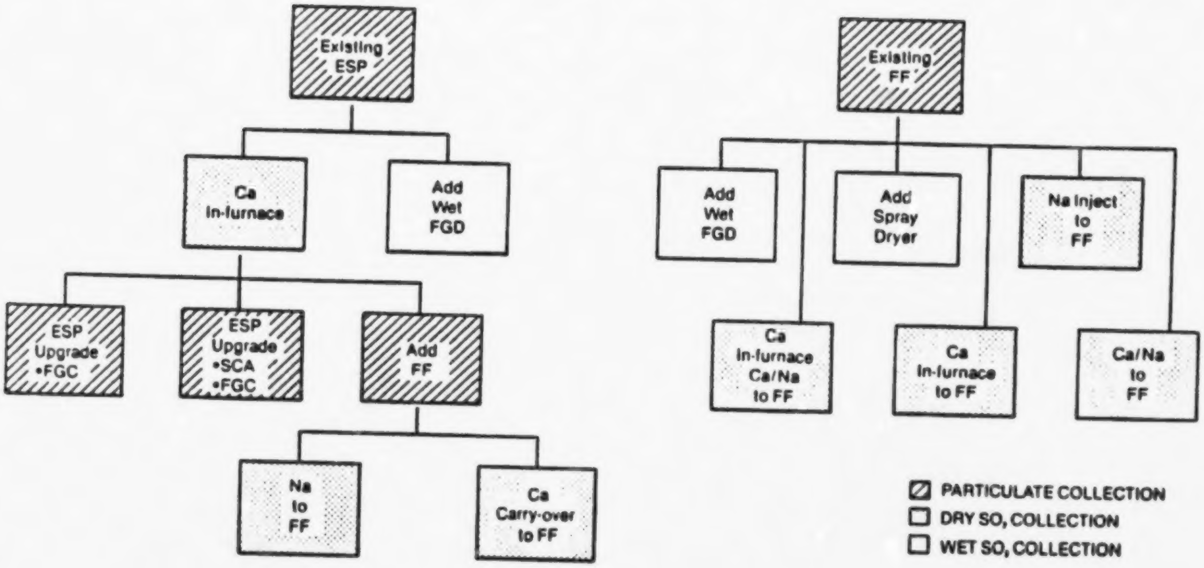

Existing ESP
Ca In-furnace
Add Wet FGD
ESP Upgrade •FGC
ESP Upgrade •SCA •FGC
Add FF
Na to FF
Ca Carry-over to FF
Existing FF
Add Wet FGD
Add Spray Dryer
Na Inject to FF
Ca In-furnace Ca/Na to FF
Ca In-furnace to FF
Ca/Na to FF
▨ PARTICULATE COLLECTION
☐ DRY SO_2 COLLECTION
☐ WET SO_2 COLLECTION

Figure 2. Commercial and developmental retrofit options for particulate and SO_2 control technologies.

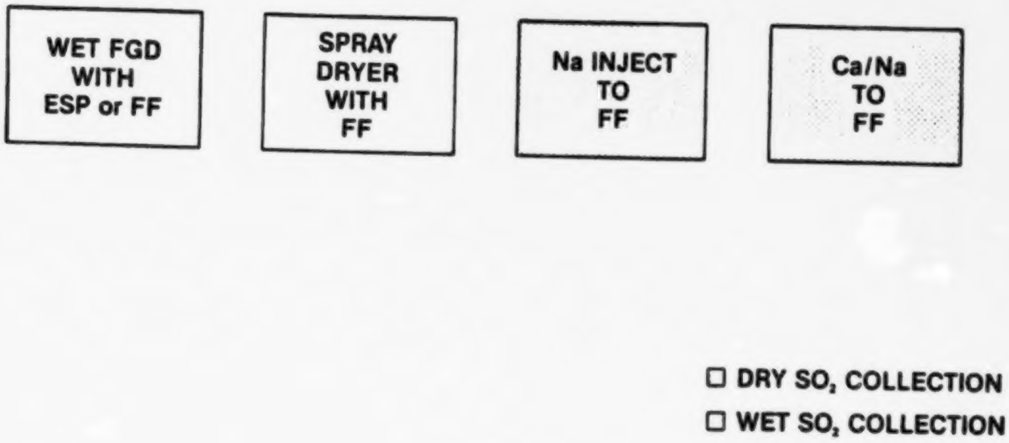

WET FGD WITH ESP or FF
SPRAY DRYER WITH FF
Na INJECT TO FF
Ca/Na TO FF
☐ DRY SO_2 COLLECTION
☐ WET SO_2 COLLECTION

Figure 3. Commercial and developmental particulate and SO_2 control options for utilities constructing new units.

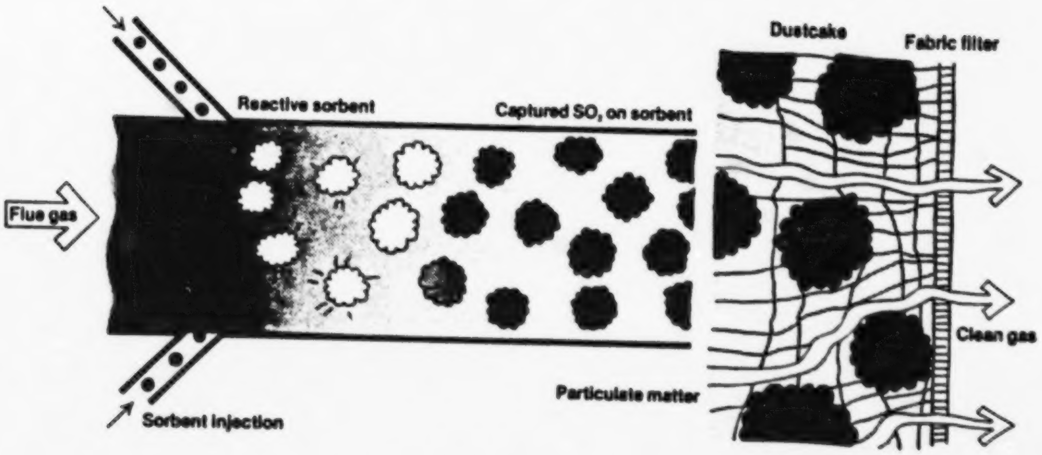

Dustcake
Fabric filter
Reactive sorbent
Captured SO_2 on sorbent
Flue gas
Clean gas
Particulate matter
Sorbent injection

Figure 4. Flue gas sodium sorbent injection -- SO_2 reaction and capture mechanisms.

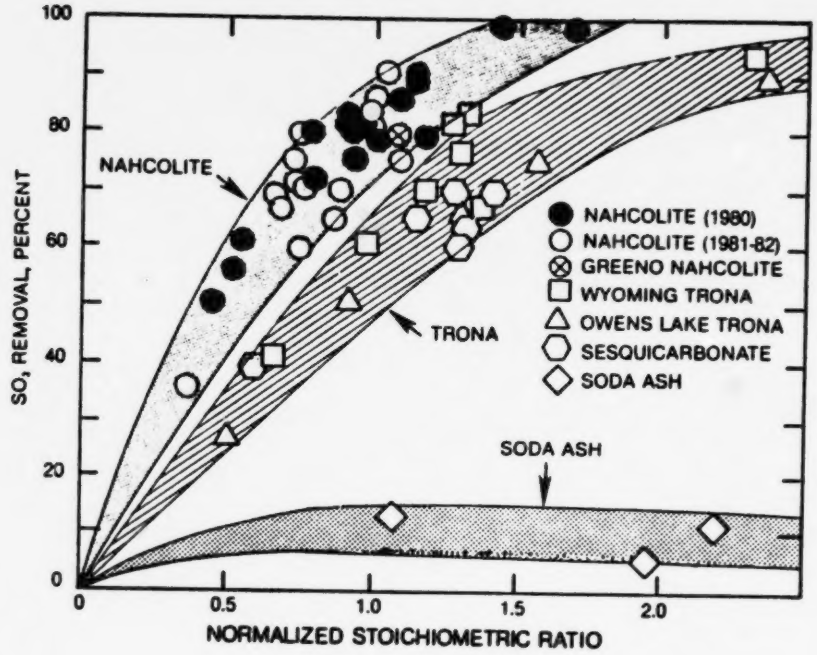
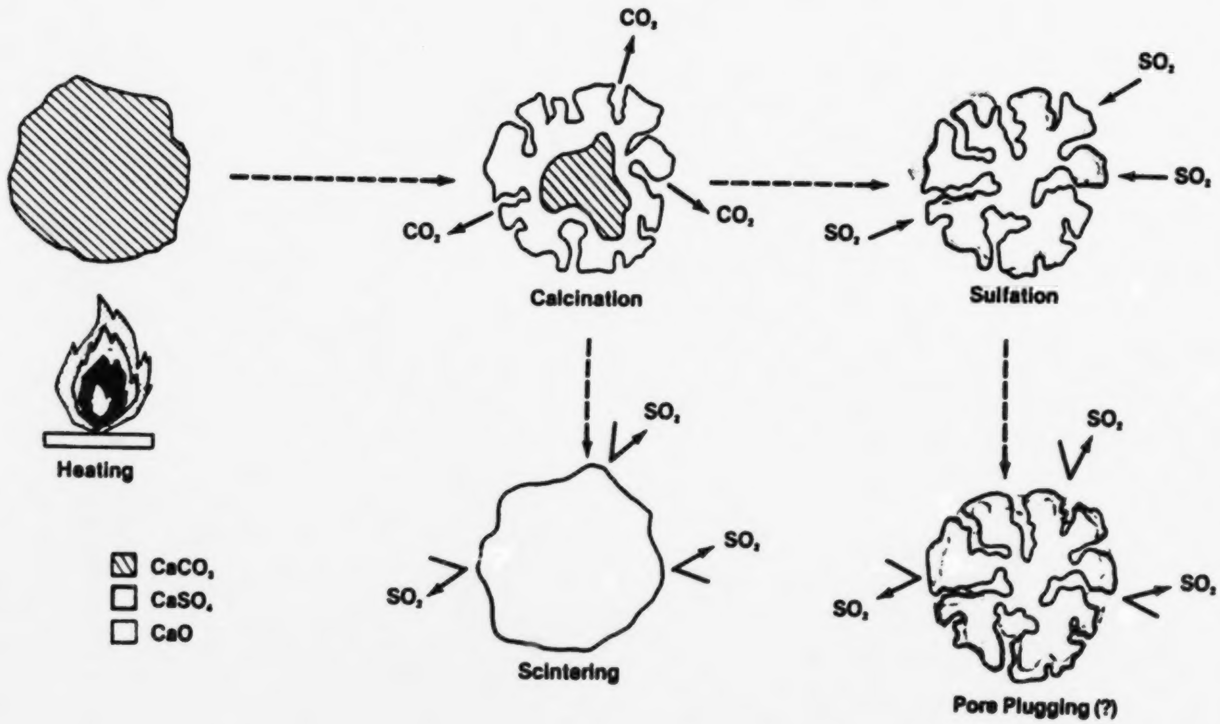


Figure 5. SO_2 removal as a function of normalized stoichiometric ratio (PSCC's 22 MW Cameo Station).



CO_2
CO_2
CO_2
SO_2
SO_2
SO_2
Calcination
Sulfation
Heating
SO_2
SO_2
SO_2
SO_2
SO_2
SO_2
▨ $CaCO_3$
☐ $CaSO_4$
☐ CaO
Scintering
Pore Plugging (?)

Figure 6. In-furnace calcium sorbent injection SO_2 capture mechanism.

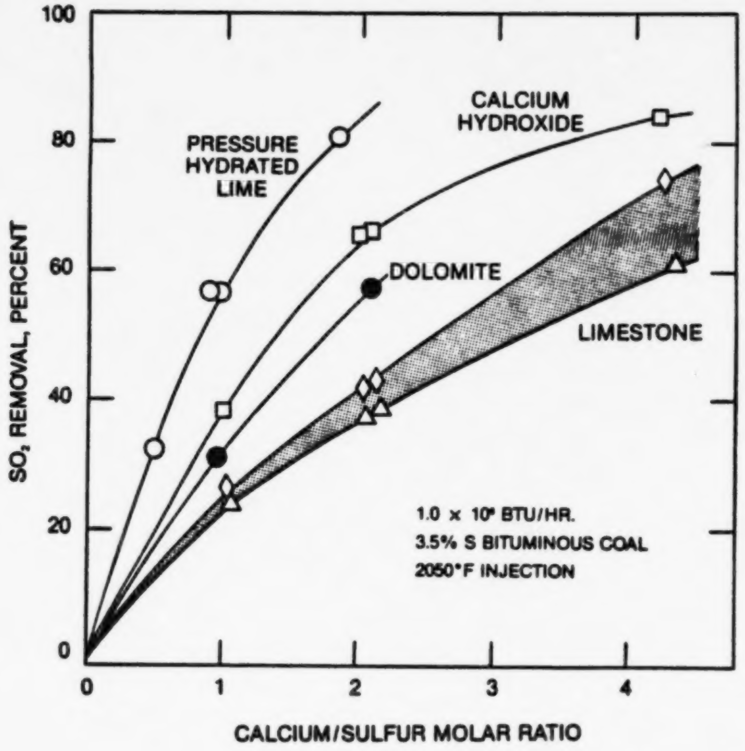


Figure 7. SO_2 removal as a function of calcium/sulfur molar ratio.

SESSION II (PART 1): FUNDAMENTAL RESEARCH

Chairman, Kerry Bowers, Southern Company Services

EPA EXPERIMENTAL STUDIES OF THE MECHANISMS OF SULFUR CAPTURE BY LIMESTONE

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ABSTRACT

Reaction kinetics of limestone particles were measured under conditions that eliminate pore-diffusion and interparticle-diffusion effects. Included in these laboratory studies were: the reaction of H_2S and sulfur with $CaCO_3$, the calcination of $CaCO_3$ to CaO, the reaction of CaO with H_2S and COS, and the reaction of CaO with SO_2. The results show that nascent lime formed immediately after $CaCO_3$ decomposition has a specific surface area of about 80 m^2/g. In all cases, the reactivity of the CaO increased with the square of the B.E.T. surface area. The reactivity is markedly affected by the presence of foreign metal oxides or salts on the CaO surface; carbonates and sulfates of the alkali metals are effective additives for promoting CaO reactivity under laboratory conditions.

INTRODUCTION

The objectives and rationale of the IERL-RTP in-house experimental studies were previously outlined at the 1982 Dallas Symposium.(1) Because sulfur capture is theoretically feasible in the reducing zone of the limestone-injection multistage burner (LIMB) and CaS formation is free of limitations on maximum conversion, our efforts began with reactions involving H_2S, using uncalcined limestone particles. Those results have been reported in detail elsewhere.(2) The second phase of work concentrated on the calcination kinetics of small limestone particles (1 to 90 μm) and measurements of B.E.T. surface area produced by "flash calcination" in the absence of CO_2. The results of that study are currently in publication.(3) The third area of investigation was reactions of CaO to form CaS under reducing conditions.(4) That work, like our subsequent studies involving CaO, was focused on the effect of specific surface area as the main experimental parameter. The reactor design developed for these studies (4, 5) is unique by the fact that particles as small as 1 μm can be examined, thus eliminating pore diffusion resistance--only under such circumstances is the surface area effect fully revealed. Elimination of diffusion resistances has also made possible, perhaps for the first time, unobscured measurements of the effect of gas phase concentration on reaction rate. These new experimental methods were also applied to the study of the reaction of CaO with SO_2 under oxidizing conditions which has been recently completed.(6)

Measurements of CaO sintering rate and the effect of reaction promoters on SO_2 capture are now in progress.

SUMMARY OF SIGNIFICANT RESULTS

Calcination

Earlier studies of the calcination kinetics of limestone particles were limited to 90-μm particle size.(7) Our objective was to examine smaller particles more appropriate to LIMB and extend the range down to 1 μm. This was accomplished with two different reactor types having very dissimilar heat- and mass-transfer characteristics. The data from both systems were correlated over a temperature range of 516 to 1000°C by a kinetic model based on the B.E.T. surface area of the undecomposed $CaCO_3$. The kinetic parameters were the same for the two diverse types of limestones evaluated: 49 kcal/mol activation energy and a rate constant of 2.5×10^{-8} mol/cm^2·sec at 670°C. The rate data were correlatable on the basis of reaction kinetics alone over a range of nearly 5 orders of magnitude.

CaO Specific Surface Area

Ishihara (8, 9) reported surface areas averaging 22 m^2/g for "instantaneous" calcination of limestone ranging from 3.4- to 49-μm particle size in an unspecified atmosphere. Coutant et al. (7), in a contemporaneous study carried out for the EPA, found CaO surface areas as high as 53 m^2/g CaO when 50-μm particles were calcined in 0.15 sec at 1230°C, dropping to about 21 m^2/g after 1.3 sec. Coutant's calcinations were made under non-isothermal conditions in combustion flue gas containing 10 percent CO_2; although the conditions were carefully controlled, the reliability of the B.E.T. measurements was uncertain due to the impossibility of completely avoiding recarbonation of CaO during sample collection. Consequently, one objective of our work was to determine CaO surface areas generated in the absence of CO_2 using nitrogen entrainment. The results showed that the specific surface area of CaO is 50-60 m^2/g when 10-μm limestone particles were calcined isothermally at temperatures up to 1075°C in 0.6 sec, and can reach 90 m^2/g when calcined at 600°C. Our results also verified that sintering occurs rapidly at higher temperatures, reducing the surface area to 25 m^2/g in an isothermal residence time of 0.5 sec at 1150°C. The conclusion reached is that the nascent CaO formed immediately after $CaCO_3$ decomposition has a grain radius, r_g, of about 150 Å and that these grains coalesce and grow at a rate that increases rapidly with temperature. The grain growth caused by this sintering process reduces the specific area, S_g, because

$$S_g = \frac{3}{r_g \, \rho_{CaO}} \qquad (1)$$

where ρ_{CaO} is the absolute density of calcium oxide.

Surface Area and Reactivity

The high specific surface area produced by rapid calcination is important to the kinetics of sulfur capture. Much of our effort has been directed toward quantitative evaluation of its importance. Early studies of low-surface area CaO (with relatively large particles) had indicated a possible linear relation between surface area and reaction rate (10), suggesting a chemically controlled process. The maximum surface area that could be produced by methods then available was less than 10 m^2/g. Using the new experimental techniques for producing nascent CaO, we have extended the kinetic measurements to a surface area of 80 m^2/g, using particles small enough to eliminate pore diffusion resistance and thus improve our ability to evaluate the surface area effect.

When pore diffusion resistance is absent, a CaO grain within a lime particle will react with a gas at a rate that is most probably controlled either by the intrinsic kinetics of the reaction at the surface of the unreacted CaO core or by diffusion through the product layer surrounding that core. The conversion (X) vs. time (t) responses expected for these respective situations are given for spherical grains by:

$$1 - (1 - X)^{1/3} = k_c t \tag{2}$$

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = k_d t \tag{3}$$

where k_c and k_d are constants for a given grain size, temperature, and gas concentration.

The conversions that we measured consistently followed the product-layer-diffusion response. As illustrated in Figure 1, the H_2S and COS reactions were adequately represented by Eq. (3) to 100 percent conversion. The SO_2 reaction also followed that response to the region where the pore volume approaches zero due to grain expansion (which will occur at X = 0.69 if particle volume is constant). In addition to Eqs. (2) and (3), the SO_2/CaO reactivity data were analyzed for three other possible controlling mechanisms: (1) first order homogeneous reaction within the grains, (2) n-th order reaction, and (3) product nucleation and growth. In no case was the data correlation superior to Eq. (3).

The derivation of Eq. (3) from Fick's law of diffusion yields the following expected relationship between k_d and r_g:

$$k_d \propto \frac{D_e}{r_g^2} \tag{4}$$

where D_e is the diffusivity of the product layer. The time required to reach a given conversion should, from Eqs. (1), (3) and (4), decrease with the square of the B.E.T. surface area if product layer diffusion controls the reaction. As shown in Figure 2, this was found to be the case. Since none of the other four possible rate-limiting mechanisms could yield more than linear dependence on S_g, we conclude that a diffusion process in the product layer determines the ultimate rate of the CaO reaction with each of the sulfur gases examined.

In addition to the high sensitivity of reaction rate to CaO surface area that is observed in the absence of pore diffusion effects, we find that the maximum conversion also increases with surface area, as indicated in Figure 3. This variable has indeed proven to be a critical reaction parameter in our studies.

Sintering

Our investigation of CaO sintering confirms the strong effect of temperature on the rate of grain growth and the resulting loss of surface area. The sintering rate of 1-μm limestone particles, after calcination under differential conditions to yield maximum initial surface area, is shown in Figure 4. The effect of temperature on the initial S_g value was weak, if at all, over the temperature range that our measurements are considered reliable: 600° to 950°C. In this range, the initial surface area was 79 ± 6 m^2/g, indicating an initial CaO grain radius of about 110 Å. Once formed, the grains grow at a rate that increases rapidly with temperature as indicated by the surface area measurements of Figure 4. A continuous flow of N_2 was passed through the reactor during these tests.

The rate of sintering is strongly affected by CO_2. This is illustrated by the data of Figure 5 which shows a series of tests in which CO_2 was added in varying concentrations to the N_2 that passed through the CaO during the sintering period. (The calcination was initially completed with a pure-N_2 sweep.) In all tests the temperature and CO_2 partial pressure were maintained well outside the region where recarbonation could occur. We conclude that CO_2 catalyzes the CaO sintering process. This effect can qualitatively account for the lower CaO surface areas found by Coutant, et al. (7) compared to the 50-60 m^2/g that we obtained by nitrogen entrainment in the EPA flow reactor. Since Coutant's calcinations were made in flue gas containing 10 percent CO_2, the lower surface areas obtained probably resulted primarily from its effect on sintering rather than recarbonation during sample collection.

SO_2 Model

Our measurements of the CaO/SO_2 reaction kinetics were correlated (6) by the following relationship:

$$k_d = 1.993\ S_g^{\ 2}\ (p_{SO_2})^{0.62}\ \exp\ (-36600/RT) \qquad (5)$$

over a range of S_g from 2 to 63 m^2/g, SO_2 partial pressures (P_{SO_2}) from 0.00012 to 0.01 atm, and temperatures (T) ranging from 1033 to 1148 K. A comparison of Eq. (5) with pilot furnace injection data of Ishihara (9) yields agreement within the expected limits of accuracy of available S_g data for high-temperature calcination in flue gas.

IMPLICATIONS OF THE KINETIC ANALYSES: RATE LIMITING MECHANISM

The above summary discusses two independent results of our studies which indicate that product layer diffusion determines the maximum rate of sulfur capture by CaO. They are: (1) the shape of the X vs. t response curves, and (2) the strong dependence on specific surface area. It should be possible to deduce the nature of the diffusion process occurring within the product layer from measurements of the effects of temperature and of gas phase concentration on the reaction rate. The obvious mode of transport would be molecular diffusion of H_2S, COS, or SO_2 through pores or cracks in the product layer. If this were so, the overall rate would be expected to increase in direct proportion to the partial pressure of the reacting gas, and the effect of temperature would be relatively slight, reflecting the 1.5-power temperature dependence of the gas diffusion coefficient. An Arrhenius-type plot of rate data for such a case would yield an apparent activation energy of only 5 kcal/mol.

The results of our investigations of the temperature effect consistently show good agreement with the Arrhenius relationship over the full range of temperatures studied: 760 to 1175°C for SO_2; and 600 to 900°C for H_2S and COS. The plots yield apparent activation energies of 37 and 31 kcal/mol, respectively, implying that the diffusing species are not gaseous. The observed results are most consistent with a mechanism of ionic diffusion in the solid state. In this case, the diffusivity of the product layer increases exponentially with temperature in the same Arrhenius relationship that defines chemical reaction rate:

$$\text{Ionic diffusion:} \quad D_e = D_o \exp(-E/RT) \qquad (6)$$

$$\text{Chemical reaction:} \quad k_c = k_o \exp(-E/RT)$$

and showing similar, high values of the activation energy, E, that normally characterize chemically controlled reactions. Without information on the independent effect of surface area on the rate of reaction, it would not be possible to distinguish between the two analogous processes.

The effect of gas concentration is also revealing. Under reaction conditions that ensure differential operation and eliminate pore diffusion, the reaction rate of CaO was found to be less than first order in all cases. For SO_2 and H_2S, the rate increased with only the 0.6 power of partial pressure. For COS, the reaction rate was independent of partial pressure as indicated in Figure 6, providing the clearest evidence against gas phase diffusion.

From the four lines of evidence discussed above, it seems most reasonable to conclude that the diffusion process controlling the rate of transport through the product layer involves the movement of ions, not gas. This conclusion is consistent with other recent investigations of CaO reactions.(11, 12, 13) Figure 7 illustrates how the solid-state process may occur: oxygen ions diffuse from the CaO core through the product layer surrounding the grains and react with the adsorbed gas at the product layer surface. The product ion counterdiffuses toward the CaO core, maintaining charge balance.

REACTION PROMOTERS

The rate of ionic diffusion is determined by the concentration of defects in the atomic lattice(14); in this case, the lattice structure of the product layer. Defects are induced either thermally--which is responsible for the exponential temperature dependence of Eq. (6)--or by the substitution of ions of different valence into the lattice. When an ion having a valence different from calcium is incorporated in the growing product layer, an oppositely charged defect is created in the lattice to preserve electroneutrality. It is characteristic of such "substitutional defects" to enhance diffusion most strongly in the lower temperature regions where thermal defects are less dominant.(15) It is not unreasonable to expect, therefore, that certain foreign metal oxides or salts might enhance the reactivity of CaO when present on its surface. If incorporated into the growing product layer, the defects induced by the foreign ions could increase ionic mobility and reduce the activation energy of diffusion through the product layer. Faster sulfur capture would result.

Cr_2O_3

Our study of promoters was begun shortly after the discovery, by the Energy and Environmental Research Corp., that Cr_2O_3 significantly enhances SO_2 capture in pilot furnace tests. When that result was confirmed by the Southern Research Institute, we undertook a laboratory study to determine: (1) if the effect of Cr_2O_3 is due to catalysis of SO_2 oxidation, and (2) whether its effect could be duplicated by other additives.

One could hypothesize that Cr_2O_3 increases the rate of SO_2 capture by any of three likely mechanisms: (1) by reducing the rate of CaO sintering, (2) by increasing the rate of SO_2 oxidation, or (3) by increasing the rate of ion diffusion. The first possibility was quickly eliminated by measurements of the sintering rate of CaO prepared from limestone containing 5 percent Cr_2O_3 additive. At 700°C, it reduced the specific surface area 60 percent relative to untreated limestone that was calcined and sintered at the same conditions. When the limestone contained only 1 percent Cr_2O_3 additive, it yielded CaO having 22 percent lower surface area.

Since Cr_2O_3 accelerates sintering, the procedure adopted to minimize this interference with the SO_2 reactivity measurements was to pre-calcine a batch of 3.0 m^2/g CaO without additive (90 min. at 980°C) then mix 9 wt percent Cr_2O_3 (equivalent to a 5 percent mixture with limestone) by grinding in a mortar. Samples of the mixture were then exposed to 3000 ppm SO_2 + 5 percent O_2 (balance N_2) in a differential reactor at 1125°C, following a 2 min. heatup period. The conversion vs. time response was compared with the response obtained with similar tests of 3.0 m^2/g CaO that was ground in the mortar, but no promoter added. A quantitative measure of the promoter's effect was determined as the ratio of k_d values (6) obtained from the two X vs. t responses.

The results of the Cr_2O_3 tests showed an increase in the reactivity by a factor of about 4.5 at 1125°C relative to the unpromoted CaO. We thus conclude that the laboratory tests do qualitatively reproduce the effect observed in field tests. Additional measurements made at a reactor temperature reduced to 800°C also showed an increase in reactivity--by a factor of about 7 compared to CaO without Cr_2O_3. Thus, high temperatures are not a requirement for "activation" by the promoter.

To determine whether Cr_2O_3 acts as an oxidation catalyst in promoting reactivity, tests were carried out in which the Cr_2O_3 (sieved to <5 μm particle size) was dispersed separately in a layer of quartz wool above the CaO sample. The gas flow thus passed through the Cr_2O_3 before reaching the CaO. No effect on the reactivity of the CaO was apparent when exposed in this manner, indicating that contact between the two solids is necessary and that the effect of Cr_2O_3 as a promoter is probably not due to catalysis of SO_2 oxidation.

Other Promoter Tests

1125°C. Tests were made with other metal oxides and salts to determine if the CaO/SO_2 reaction can be promoted by substances besides Cr_2O_3. Table 1 lists those screened so far. The test procedure was the same as described above (1125°C, 9 wt percent promoter added to 3.0 m^2/g CaO). Since most of these measurements are preliminary, differences less than 20 percent should not be considered significant.

Comparisons of Table 1 data show that the carbonates and sulfates of the alkali metals are as effective as Cr_2O_3 in promoting the SO_2 reaction with CaO under the conditions of our tests.

Included in the list are V_2O_5 and Fe_2O_3, both known catalysts of SO_2 oxidation. Their low effectiveness as CaO reactivity promoters, compared to non-catalysts such as Na_2SO_4, is further evidence that catalysis is not involved in the mechanism.

Table 1 also shows that Cl^- ion inhibits the reaction; both NaCl and $FeCl_3$ reduced reactivity while compounds containing the same cations, but no Cl^-, increased reactivity. Earlier experiments (2) have shown that $CaCl_2$ is a strong inhibitor of the $H_2S/CaCO_3$ reaction under anoxic conditions, suggesting a mechanism similar to the one operating here.

Figure 8 shows the effect of varying the amount of promoter added for Na_2CO_3. The doses were equivalent to 1, 2, and 5 wt. percent addition to limestone. The degree of enhancement increased with the amount added, but not in direct proportion. It is important to note that the contribution of the Na_2CO_3 to SO_2 capture is relatively minor: at the 5-percent level of additive, it accounts for about 7.5 percent of the total sulfur capture while the CaO conversion doubled.

800°C. If promoters function by the lattice-defect mechanism, a reduction of the activation energy should be apparent. Another series of tests was therefore conducted at 800°C to permit comparisons with the reactivities measured at 1125°C. These tests were focused on elements of Group IA of the periodic table which were identified as potentially most effective by the initial screening at 1125°C. Figure 9 shows the conversion vs. time responses measured for several of these additives. Table 2 lists the k_d ratios obtained from the curves by the same methods used for the Table 1 data. Comparison of the tables shows that the ratios are all significantly greater at low temperature, in accordance with the expected reduction in activation energy. The effect of Li_2CO_3 was most striking, increasing the CaO reactivity to such an extent that 100 percent conversion was attained. Additional response curves were measured for Li_2CO_3 at 1000°, 900°, and 700°C all of which showed little difference from those at 800° and 1125°C. The activation energy is apparently reduced to near-zero by Li_2CO_3 in this temperature range.

The effect of Cr_2O_3 on CaO sintering has been discussed. Additional tests were made to evaluate the relative rates of sintering caused by other promoters. These tests were conducted at 800°C, adding 5 wt percent of the promoter to <3 μm limestone particles and calcining under differential conditions; the CaO was then sintered without nitrogen flow for 10 min. Table 3 shows the preliminary results; it is apparent that accelerated sintering is a common feature of most potential additives. At this stage of our investigations, one would expect the most effective promoter to be that with highest overall ranking in Tables 1, 2, and 3.

CONCLUSIONS

In the absence of pore diffusion and interparticle diffusion resistances, the reactivity of CaO with H_2S, COS, or SO_2 increases with the square of the specific surface area.

When surface area is constant and pore diffusion resistance is absent, the reactivity of CaO increases exponentially with temperature in accordance with the Arrhenius relationship. The apparent activation energies are 31 kcal/mol for H_2S and COS, and 37 kcal/mol for SO_2.

The ultimate rate of reaction is determined by diffusion through the product layer surrounding the CaO grains within a calcine particle.

Diffusion through the product layer appears to occur by a solid-state process involving ionic transport, not by gas diffusion.

The reactivity of CaO with SO_2 can be markedly affected by the presence of foreign metal oxides or salts on its surface.

The observed effects of promoters are not consistent with a mechanism involving catalysis of SO_2 oxidation. The effects are qualitatively consistent with a mechanism which assumes that defects are induced in the growing product layer, increasing the ionic diffusivity.

Carbonates and sulfates of the alkali metals were the most effective practical promoters found to date, according to the screening procedures used in our laboratory.

The reactivity of CaO with COS is zero order with respect to COS concentration.

CaO sintering is accelerated by CO_2 and by most promoters of the CaO/SO_2 reaction.

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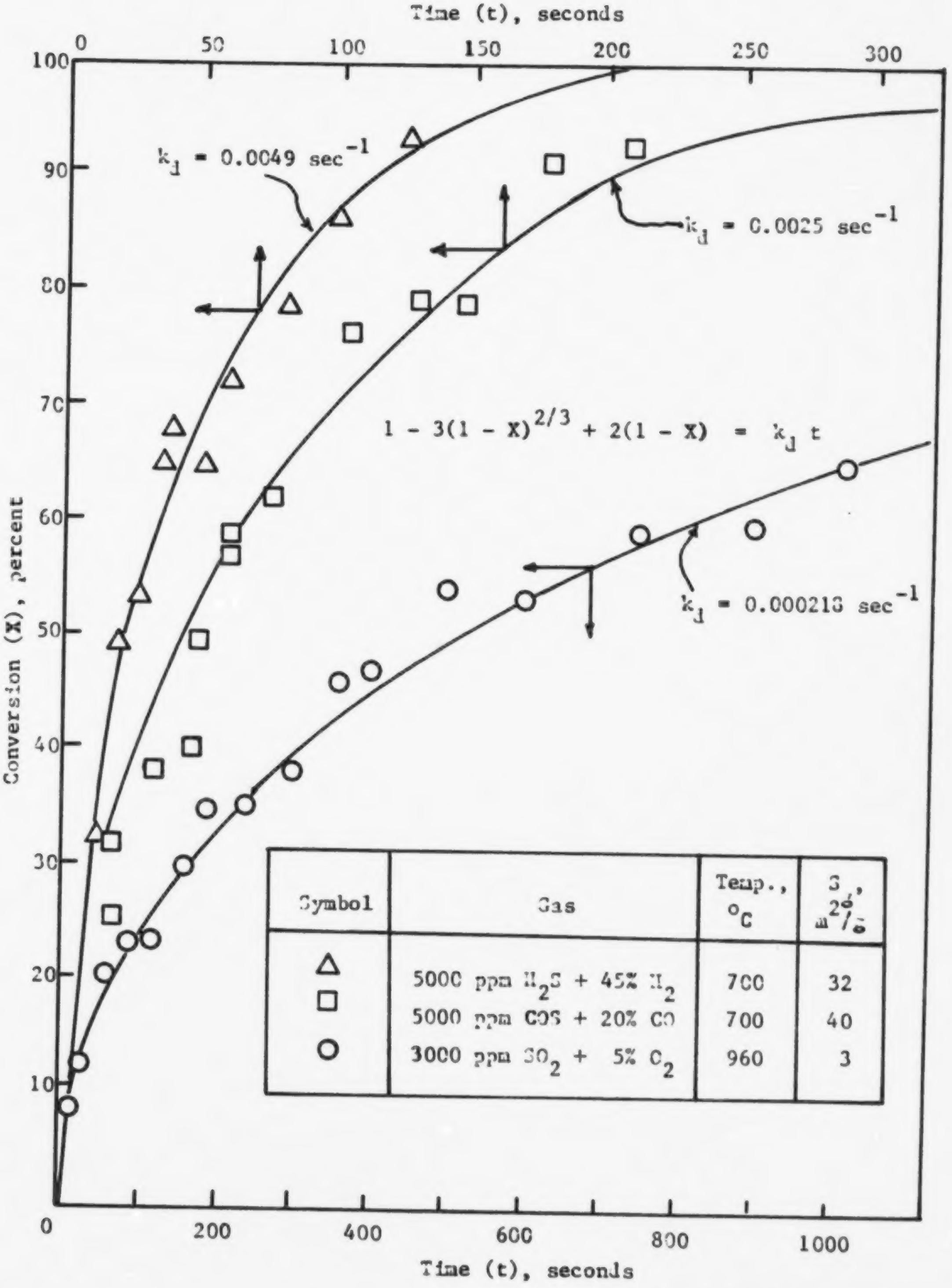

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Figure 1. Response characteristics of the reaction of 1-μm CaO particles with sulfur gases.

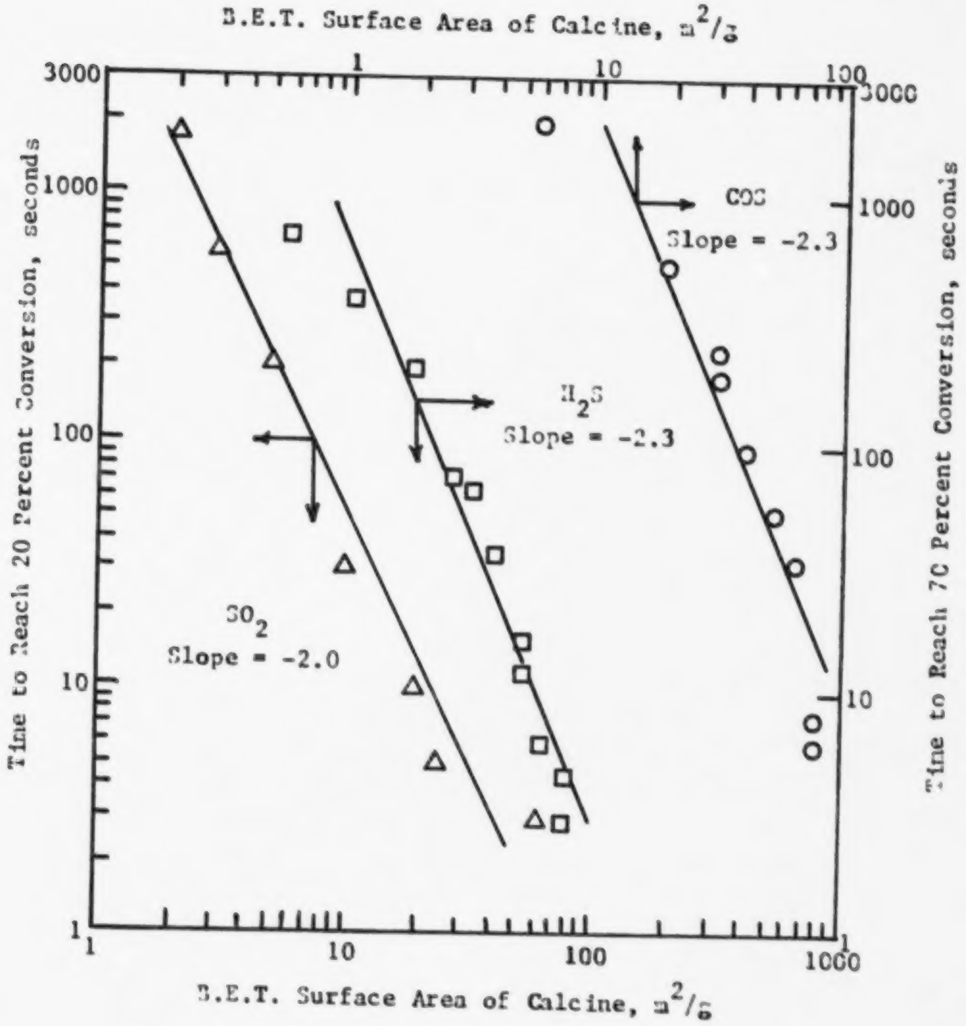

Figure 2. Test for product-layer diffusion control.

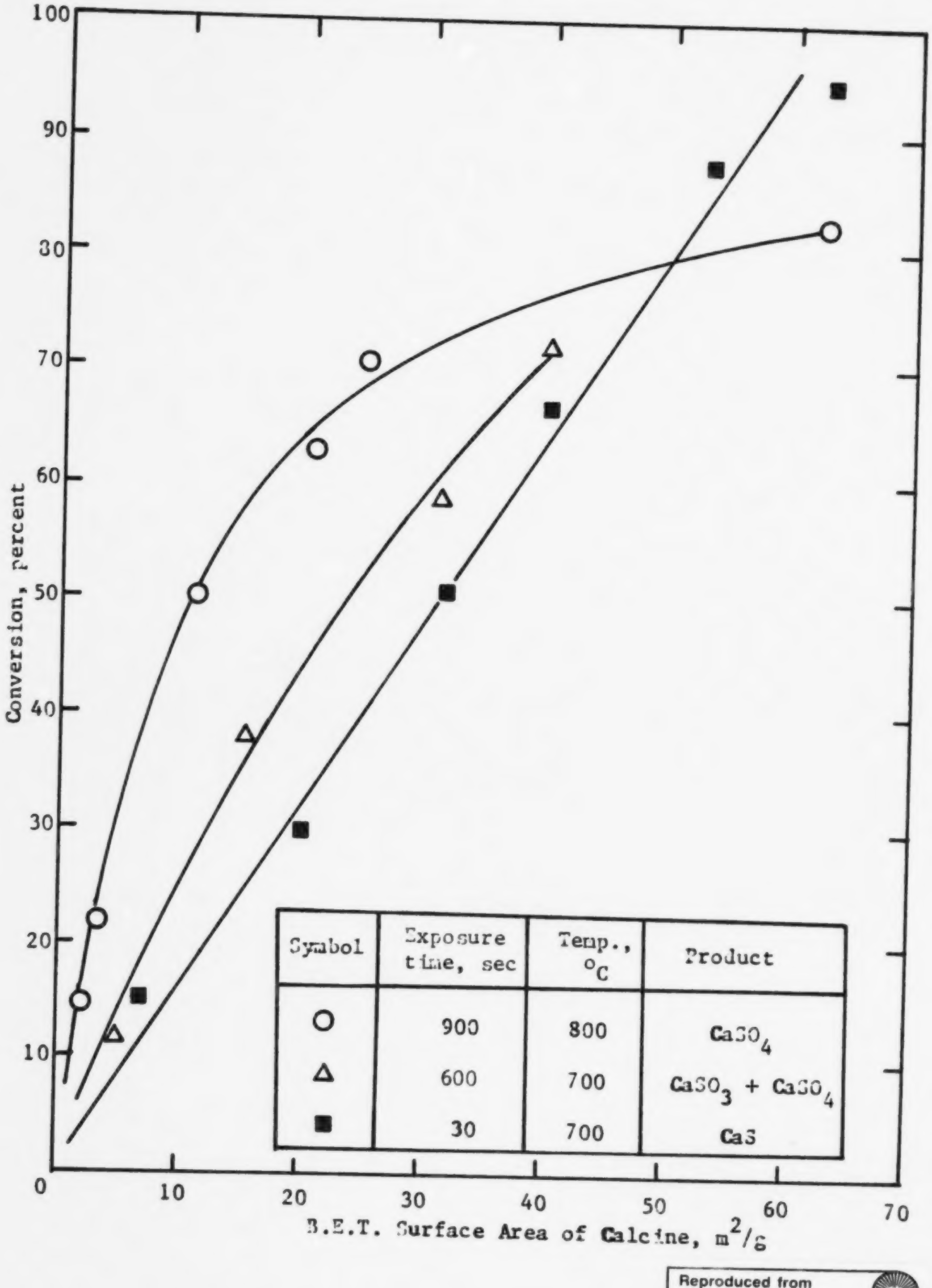

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Figure 3. CaO conversion as a function of its initial specific surface area. Closed symbols = 5000 ppm H_2S + 45% H_2. Open symbols = 3000 ppm SO_2 + 5% O_2.

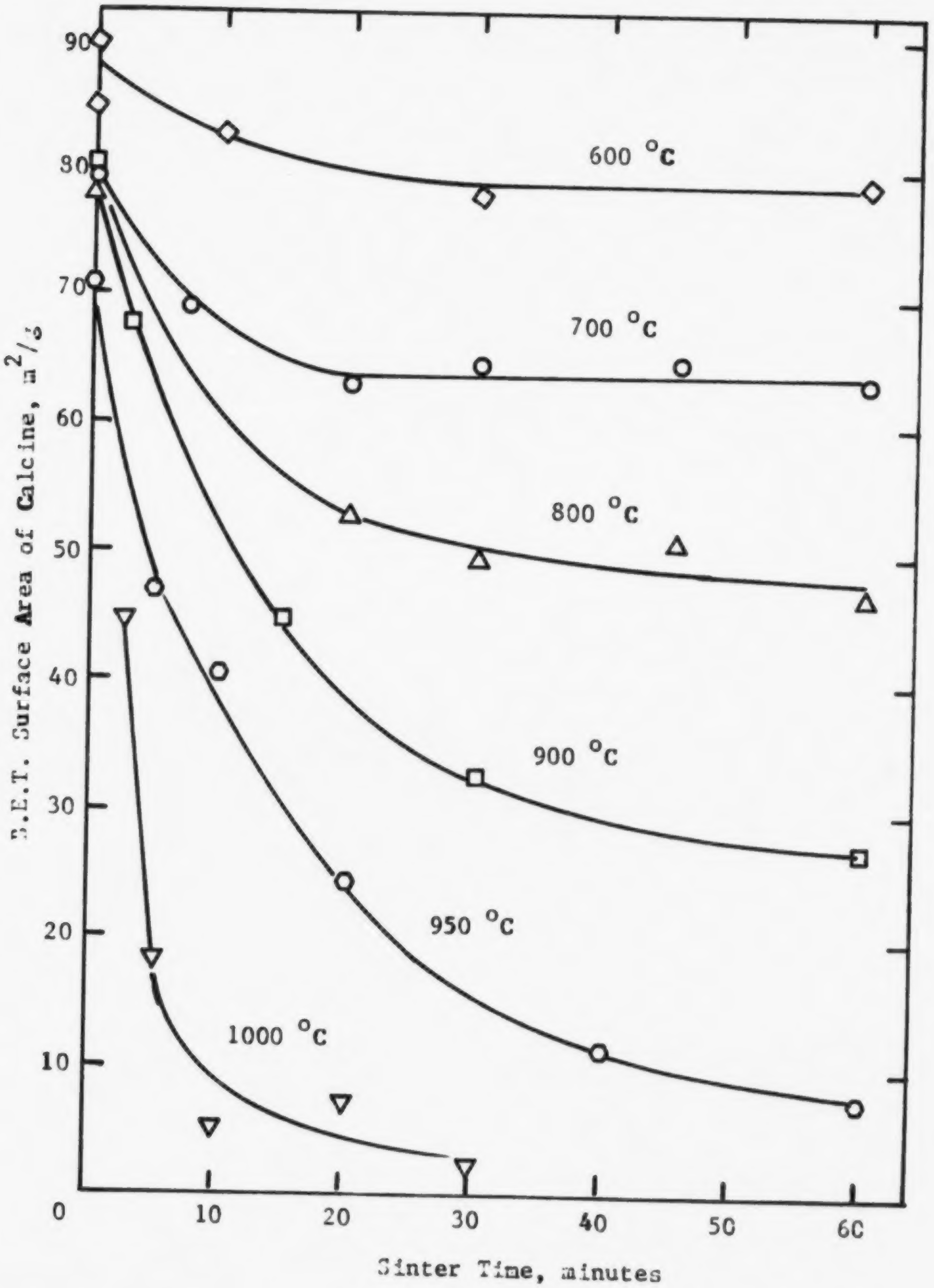

Figure 4. Sintering rate of CaO in the differential reactor. Pure nitrogen sweep during sinter period.

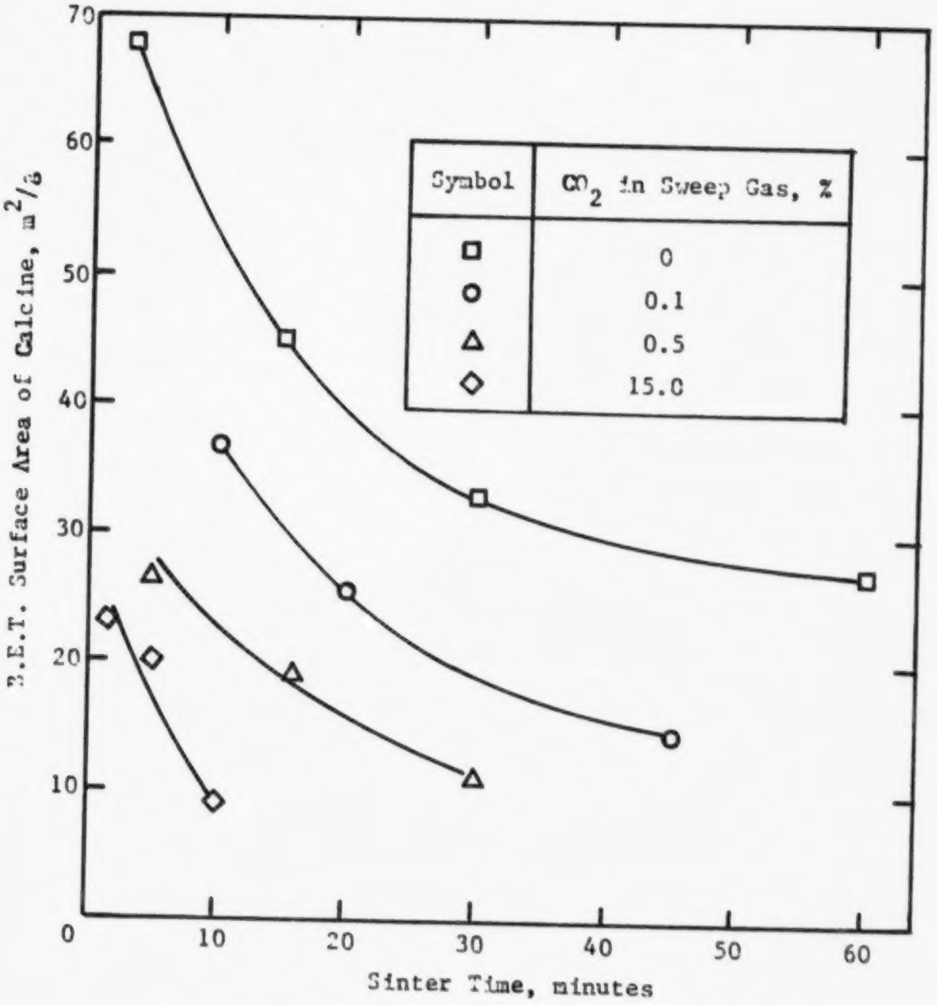

Figure 5. Effect of CO_2 on the sintering rate of CaO at 900°C.

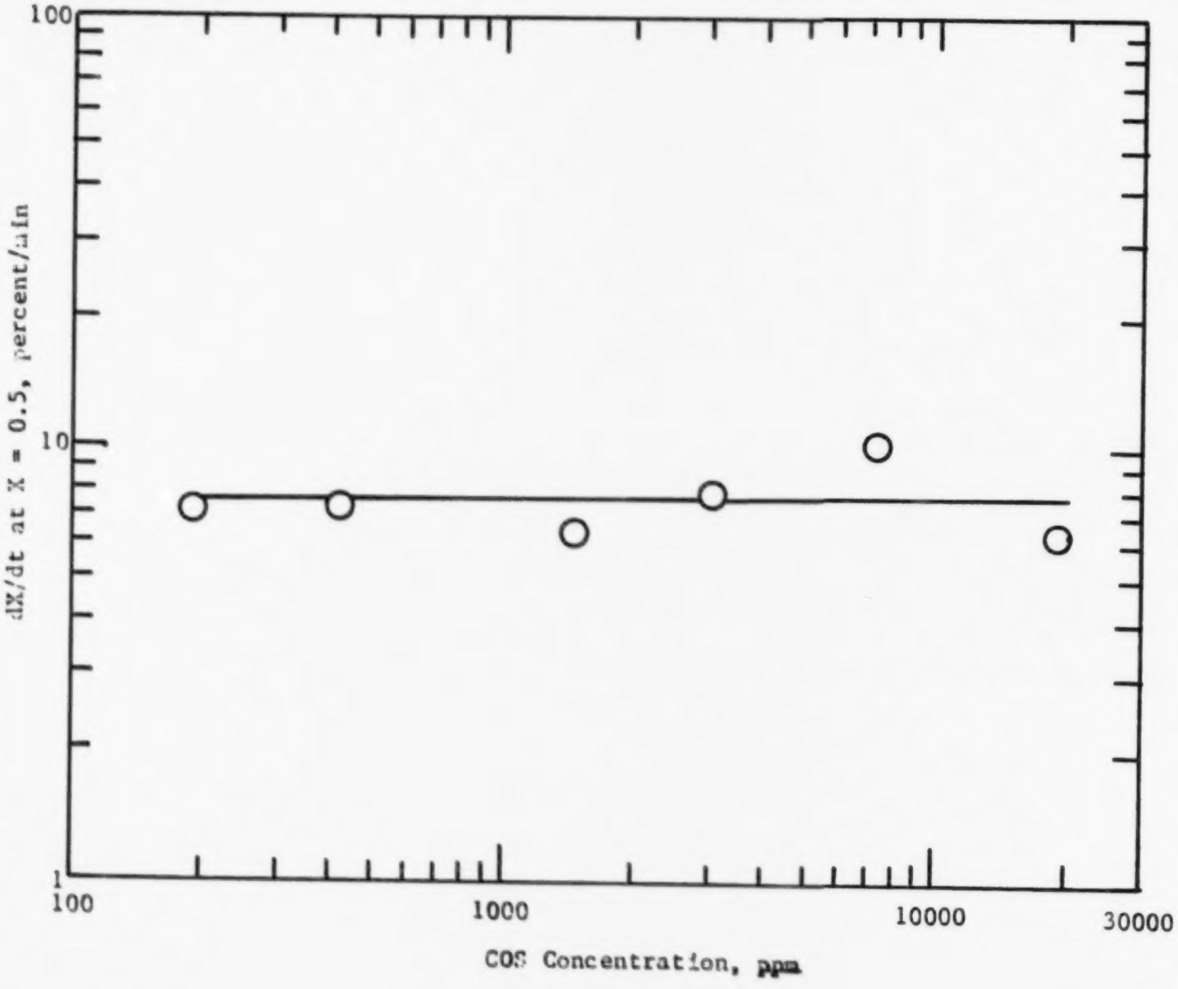

Figure 6. Reaction rate of CaO with COS as a function of gas-phase concentration. Temperature = 700°C.

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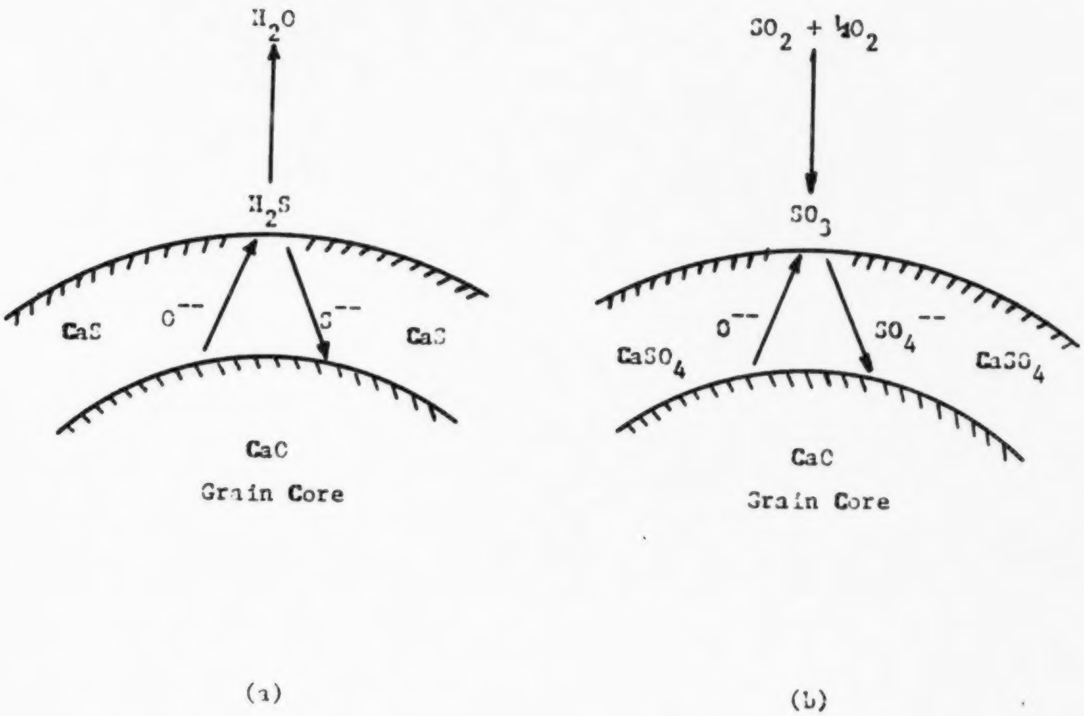
H_2O
H_2S
CaS
O^{--}
S^{--}
CaS
CaO
Grain Core
(a)
$SO_2 + \frac{1}{2}O_2$
SO_3
O^{--}
SO_4^{--}
$CaSO_4$
$CaSO_4$
CaO
Grain Core
(b)

Figure 7. Possible mechanism of ionic diffusion in the product layer: (a) H_2S reaction, (b) SO_2 reaction.

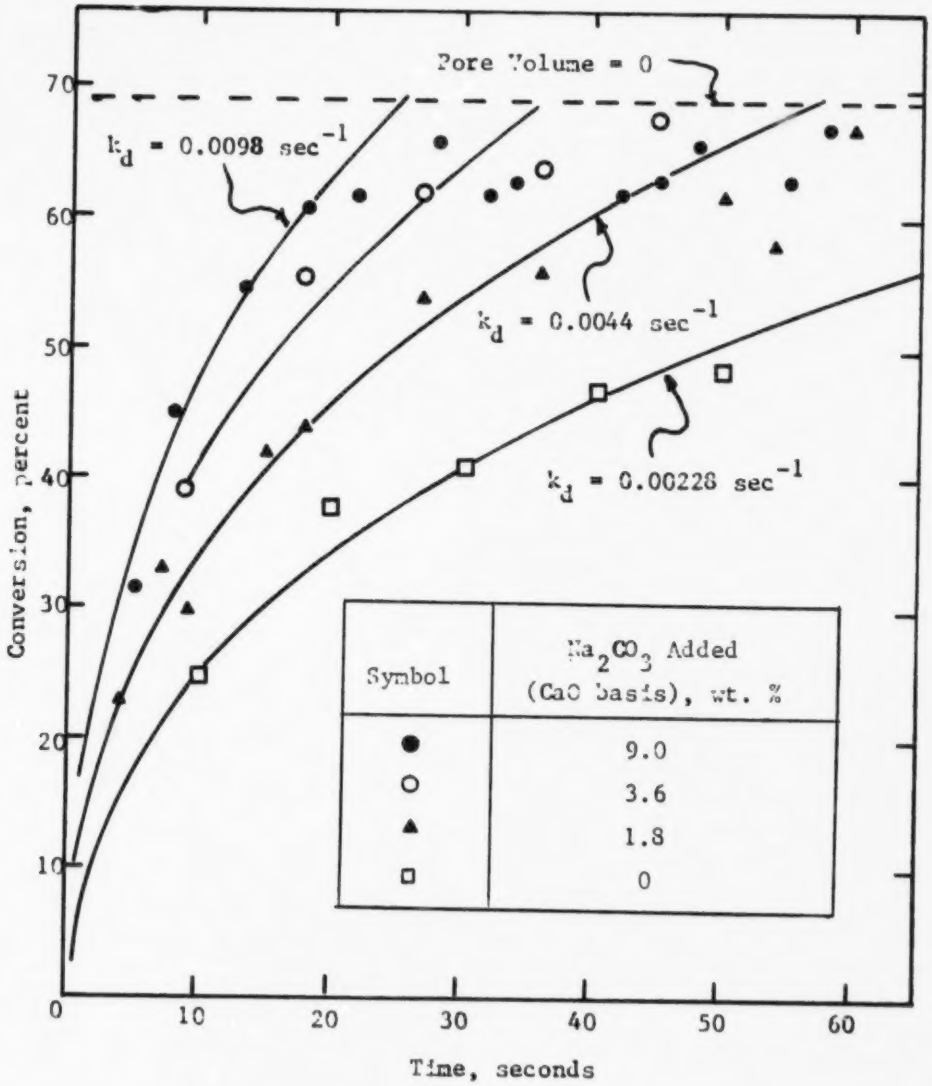

Figure 8. Effect of sodium carbonate on the reactivity of 3.0-m^2/g CaO at 1125°C. 3000 ppm SO_2 + 5% O_2.

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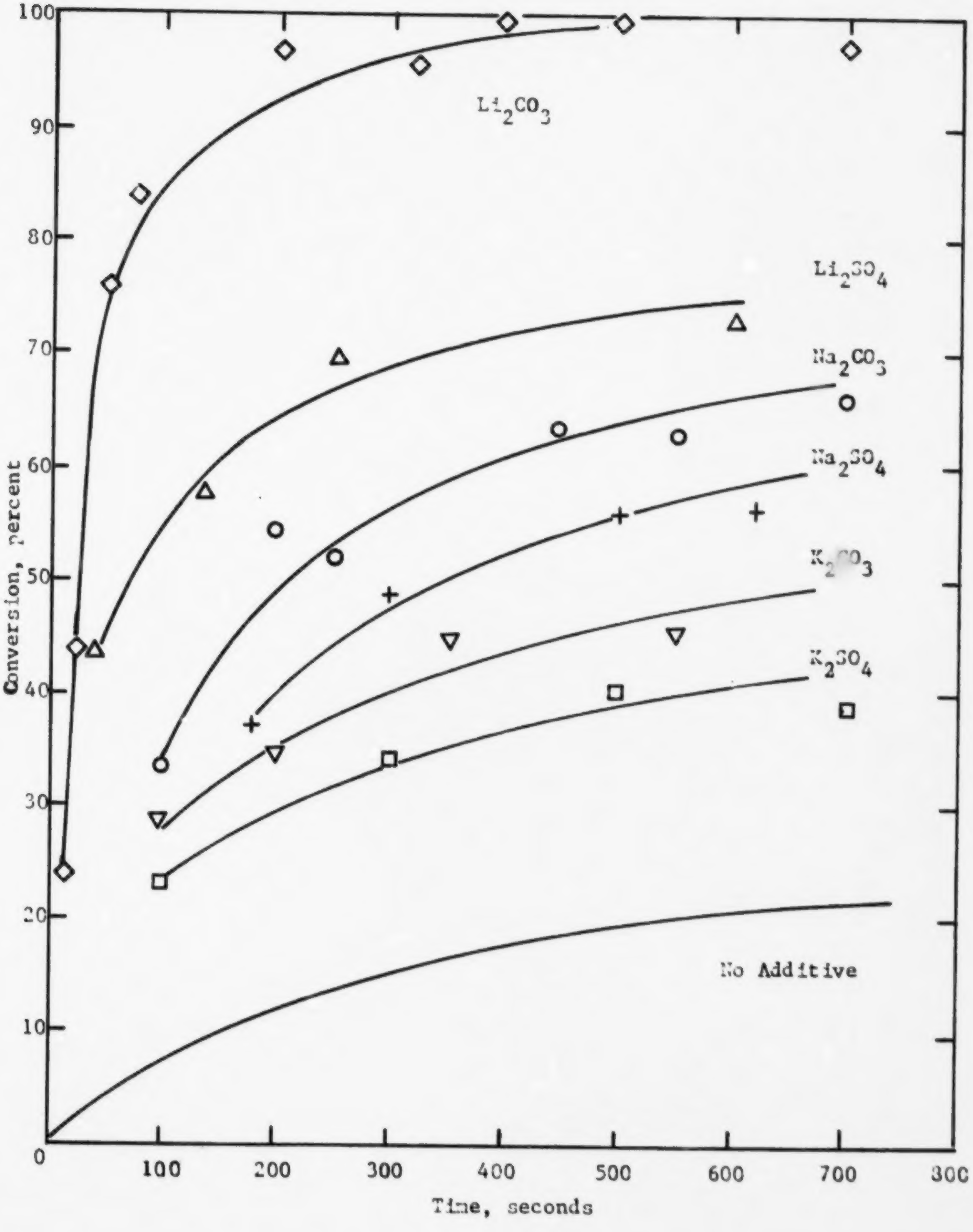

Figure 9. Comparison of the effect of alkali-metal salts on the reactivity of 3.0 m^2/g CaO at 800°C. Additive = 9 wt. %, CaO basis (5% limestone basis). 3000 ppm SO_2 + 5% O_2.

Table 1

PROMOTER SCREENING TESTS AT 1125°C

(9 wt. percent in 3.0 m^2/g CaO, 3000 ppm SO_2 + 5% O_2)

Additive	Ratio $\frac{k_d \text{ With Additive}}{k_d \text{ Without Additive}}$
Rb_2SO_4	4.6
Cr_2O_3	4.5
Na_2CO_3	4.3
Rb_2CO_3	4.2
K_2SO_4	4.1
$NaHCO_3$	4.0
$NaHSO_4$	4.0
K_2CO_3	4.0
$Na_5P_3O_{10}$	3.9
Na_2SO_4	3.7
Trona	3.5
$KHCO_3$	3.0
Na_2SiO_3	2.5
MoO_3	2.3
$Li_2SO_4 \cdot H_2O$	2.2
TiO_2	1.9
H_3BO_3	1.8
$NiCO_3$	1.8
$Na_2B_4O_7$	1.6
P_2O_5	1.6
Fe_2O_3	1.4
Al_2O_3	1.4
Silicic Acid	1.3
MgO	1.2
Li_2CO_3	1.1
V_2O_5	1.1
ZnO	1.0
None	1.0
Sb_2O_5	0.8
CuO	0.8
NaF	0.7
NaCl	0.4
$FeCl_3$	0.3
NaBr	0.2

Table 2

PROMOTER TESTS AT 800°C
(9 wt. percent in 3.0 m^2/g CaO, 3000 ppm SO_2 + 5% O_2)

Additive	Ratio $\frac{k_d \text{ With Additive}}{k_d \text{ Without Additive}}$
Li_2CO_3	200
$Li_2SO_4 \cdot H_2O$	59
$Na_5P_3O_{10}$	21
Na_2CO_3	20
Na_2SO_4	13
$KHCO_3$	13
Rb_2CO_3	11
K_2CO_3	9
K_2SO_4	8
Cr_2O_3	7
$NaHCO_3$	6

Table 3

SINTERING TESTS OF SO_2-REACTION PROMOTERS
(5 wt. percent in limestone, calcined and sintered at 800°C)

Additive	CaO Specific Surface Area (m^2/g)
None	37
Al_2O_3	30
MoO_3	23
Na_2CO_3	20
Na_2SO_4	18
Na_2CO_3 (repeat)	17
$NaHCO_3$	15.0
$NaHCO_3$ (repeat)	15.2
Rb_2CO_3	13
K_2CO_3	12
Cr_2O_3	11
Li_2CO_3	1.4
Li_2CO_3 (repeat)	4.2

FLOW REACTOR STUDY OF CALCINATION AND SULFATION*

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ABSTRACT

The renewed interest in direct furnace injection of dry sorbents for SO_2 control from coal fired boilers has prompted bench scale studies of the calcination and sulfation of calcium compounds. The bench scale study was conducted in a one-dimensional flow reactor. The objective of the study was to determine the interrelationships of the calcination and sulfation processes and how these processes are influenced by the type of sorbent material, temperature, and residence time. Four materials were studied: two limestones, a calcium hydroxide, and a pressure hydrated dolomitic lime. Calcination and sulfation of these sorbents were investigated over the temperature range of 1400-2000°F and residence times of 0.20 to 0.75 seconds. The reaction environment consisted of combustion products from a natural gas or hydrogen fired burner doped with SO_2 and CO_2.

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**Currently with the Fossil Energy Research Corporation

FLOW REACTOR STUDY OF CALCINATION AND SULFATION

INTRODUCTION

Dry sorbent emission control is currently undergoing renewed interest as an SO_2 control approach for coal fired boilers. While this technology was investigated during the 1960's and early 1970's the results were unsuccessful in achieving NSPS goals. Success of this current development activity hinges on gaining a better understanding of the process fundamentals. EPRI and Southern Company Services are currently supporting the development of dry sorbent emission control (DSEC).

At the onset of the program, little fundamental information existed on the fundamentals of the calcination and sulfation processes for conditions representative of utility boilers. Previous studies (Ref. 1-5) had studied calcination and sulfation using rather large particles and in experimental systems with either characteristically long residence times; or in pilot scale systems where the conditions were not uniform or well specified. To support the current development program, bench scale experiments were conducted to provide a fundamental basis to interpret the pilot scale work being conducted as part of the DSEC development program.

The objective of the study was to develop an understanding of the interrelationship between the calcination and sulfation processes and the effects of temperature and residence time on the processes for a variety of calcium based sorbents. This was considered important in gaining an understanding of the mechanisms that either limit high sorbent utilization or can be taken advantage of in yielding high utilization in a utility boiler environment. In particular the bench tests were structured to determine: (1) the rate of calcination of both limestones and calcium hydroxides in an idealized combustion gas environment; (2) the evolution of surface area of the calcine during the calcination process; and (3) the rate of sulfation as a function of temperature, residence time, and sorbent type.

EXPERIMENTAL APPARATUS

A one dimensional entrained flow reactor was used for the study. A schematic diagram of the experimental apparatus is shown in Figure 1. The system is comprised of an isothermal flow reactor, a sorbent injection system, and a sampling system. The flow reactor (Figure 2) consists of a 1.94 inch (I.D.) stainless steel tube, three feet long, which is heated electrically. The reactor was operated with the inside diameter defined by the stainless steel tube or lined with a high alumina refractory. The electrical heaters were controlled using thermocouples located in the reactor gas stream. A gas burner, using either natural gas or hydrogen, was used to generate gases for the reactor. In addition a variety of dopant gases, typically CO_2 and SO_2, were added to the gas stream at the burner. The temperature at the entrance to the reactor test section was controlled by varying the location of the burner in the horizontal section and by the electrical heaters on the horizontal section (Figure 2).

Temperatures within the test section were controlled by the electrical heaters. In the current configuration the flow reactor could be operated over the temperature range of nominally 1200°F-2100°F. All flows to the reactor were measured with calibrated rotameters.

The flow reactor is operated at a flowrate of approximately 1.4 scfm, which at a temperature of 1800°F results in a velocity of 6.5 ft/sec and a residence time over the maximum reactor length of 0.75 seconds. Residence time was varied by varying the reactor length from 1.5 to 3 feet or varying the gas flow through the reactor.

A fluidized bed feeder was used to feed the sorbents to the reactor. Two fluidized bed feeder designs were used; a mechanically fluidized system similar to that employed by Borgwardt (Ref. 6) or a sprouted fluidized bed that was mounted on a load cell. This latter arrangement could be used to more accurately determine the sorbent feed rate. For the results reported in this paper sorbent feed rates were on the order of 10 grams/hr. The sorbent was injected into the reactor through a water cooled injector to insure that all reaction occurs within the test section.

The sorbent sampling system is comprised of a sample probe, particle collector, vane pump and a gas sample system. The probe is water cooled with the capability of injecting inert gas into the sample stream to quench the reactions. All of the reactor gas flows through the sample probe. The solid sample is collected with either a cyclone or an alundum thimble. A gas sample is extracted upstream of the solids collector and is continuously analyzed for O_2, CO_2, CO and SO_2.

Basically two types of experiments were conducted during the study:

- Calcination experiments where the flow reactor was operated without SO_2 and the rate of calcination and the evolution of calcine surface area determined.
- Sulfation experiments where SO_2 was added to the flow reactor gas stream and the extent of sulfation determined. During these tests the flow reactor was operated in a dilute mode where the Ca/S ratio was much less than unity. In this way the sorbent particle was exposed to a constant SO_2 concentration over the entire residence time in the reactor test section.

All data analysis was based on characteristics of the collected solids. The solids were analyzed for carbon and hydrogen with a Perkin-Elmer elemental analyzer and the sulfate content determined by ion chromatography*. The extent of calcination of the calcium carbonate materials was determined from the carbon content of the sample and calcination of the hydrated sorbents determined from the hydrogen concentration of the sample. The extent of sulfation (or sorbent utilization) was determined from the sulfate content.

The BET surface area of the samples was measured using a Micromeritics Flow Sorb analyzer. This instrument performs a single point determination of the BET area.

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* Chemical analysis of the samples were perfomed by the Southern Research Institute.

SORBENT CHARACTERISTICS

A variety of sorbents were used during the study including two natural limestones, a calcium hydroxide, and a pressure hydrated dolomitic lime. These same sorbents are being used in a pilot scale study of dry sorbent emission control (Ref. 7). The chemical and physical properties of the sorbents are given in Table 1. The two limesones were selected to represent a range of morphological properties. The St. Genevieve limestone is a fairly crystalline material with a surface area of 1.7 m^2/gm while the Marianna limestone has a substantially higher initial surface area, 6.3 m^2/gm. The $Ca(OH)_2$ and pressure hydrated dolomitic lime were selected as being typical, commercially available, hydroxide compounds.

RESULTS

The test program involved separate tests of the calcination and sulfation of the sorbents. These results will be discussed separately below. It should be pointed out that the test program is currently ongoing and the results presented in this paper should be viewed as preliminary.

Calcination

The calcination results of the tests performed with the St. Genevieve limestone in a flue gas environment containing 12 percent CO_2 are shown in Figure 3a. As expected the calcination rates increase as a function of temperature. At 2000°F 80 percent of the calcination occurred in less than 0.5 seconds. The Marianna calcined more rapidly (80 percent in 0.3 seconds at 2000°F) and shows similar temperature dependence with increasing calcination rates with increasing temperature. Both, the Marianna and the St. Genevieve limestones exhibit no calcination at 1400°F in an environment of 12 percent CO_2. This is expected since the equilibrium partial pressure of CO_2 at 1400°F is 0.12 atm. Removing the CO_2 from the gas stream (by firing hydrogen) results in calcination of the limestone at 1400°F as shown in Figure 4. At a temperature of 1800°F changing the bulk gas CO_2 concentration from 0 to 12 percent has no apparent effect on calcination. Again this result is expected since the equilibrium partial pressure of CO_2 for the calcination reaction is 0.8 atm at 1800°F.

Borgwardt (Ref. 6) suggested that in a kinetically limited regime calcination rates are proportional to initial BET surface area with an activation energy of 48 Kcal/moles. For the conditions studied in this program the higher surface area stone calcined more rapidly even though the particle size of the Marianna limestone was 3.5 times as large as the St. Genevieve stone. However, both the Marianna and St. Genevieve stones exhibited slower calcination rates than reported in Ref. 6. The porosity of these stones may have resulted in a CO_2 diffusion limitations within the particle which lowered the overall rate of calcination relative to kinetic limitations.

Figure 5 shows the results of the calcination tests with calcium hydroxide. From these results it is not possible to identify any temperature dependence of the calcination rate. This is thought to be an artifact of the analysis since the degree of calcination is determined by the mass fraction of hydrogen which accounts for only three percent of the total mass of the uncalcined material. Any contamination by moisture or modest error in the analysis results in relatively large discrepency in the calculated degree of calcination. It is evident, however, that the calcination rate of the calcium hydroxide is faster than that of the limestones with at least 80 percent calcination occuring in 0.2 seconds. The pressure hydrated dolomitic lime exhibited calcination rates comparable to the calcium hydroxide.

The evolution of surface area for the Marianna limestone (Figure 6) shows that the surface area of the material increases with reactor residence time to a peak value and then decreases. Highest surface areas are generated at the lower temperature conditions. During calcination the surface area increased by over a factor of about two (from 6.3 m^2/gm to 15 m^2/gm).

The surface area of the pressure hydrated dolomitic lime (Figure 7a) is seen to be an increasing function of reactor residence time during calcination. The evolution of surface area is also seen to be a function of reactor temperature with surface areas of 37 m^2/gm being produced at 1800°F and residence times of 0.6 seconds. This effect is not observed during the calcination of calcium hydroxide. Figure 7b shows that the BET surface area for the calcium hydroxide does not increase as a function of residence time but actually decreases somewhat. Since calcination results with the calcium hydroxide were not obtained for residence time less than 0.2 seconds, higher surface areas could have been produced early in the calcination process and that grain growth and sintering of the porous CaO structure occurred at residence times earlier than 0.2 seconds.

Calcination of the pressure hydrated dolomitic lime in the flow reactor resulted in substantial increases in BET surface area (Figure 7a). To investigate the effect of more moderate heating on surface area, small quantities of the material were heated at temperatures of 300-400°C for 16 hours in a nitrogen sweep gas. The resulting weight loss and BET surface areas are shown in Figure 8a and 8b respectively. As seen in Figure 8a, the majority of the weight loss can be associated with the dehydration of one water molecule from the dolomitic hydroxide (a somewhat greater weight loss occurred with heating at the 400°C condition). Thermodynamic considerations suggest that the dehydrated water is associated with the magnesium. Surface areas in excess of 110 m^2/gm resulted from the heating process. Further, data at 350°C and 400°C suggest that the surface area continues to increase up to the point where the one H_2O molecule is dehydrated. With further heating and weight loss (heating times greater than nine hours at 400°C) the surface area begins to decrease. Sulfation tests of these partially precalcined materials is currently in progress.

Sulfation

Sulfation of the sorbents was investigated over the same conditions as the calcination tests. During these experiments, the sorbent feed rate was kept at a value such that $Ca/S < 1$ in order that the sorbent particle experienced a constant SO_2 level throughout its residence time in the reactor. In general, the sulfation data exhibited a higher degree of variability than the calcination data, and the source of this variability is still under investigation. The results of the sulfation of the Marianna limestone and calcium hydroxide are shown in Figure 9a and 9b respectively. For the sulfation of Marianna limestone two points are noteworthy. First, the general level of calcium utilization (e.g., fraction of the calcium converted to sulfate) is on the order of 15 to 20 percent. Secondly, there is very little effect of temperature over the range of 1600 to 2000°F. The effect of residence time is difficult to establish although it appears that beyond 0.25 seconds, the utilization only increases by about 15-17 percentage points per second. More data is needed to more definitively establish the residence time effects.

The sulfation of the calcium hydroxide, shown in Figure 9b exhibits a somewhat higher utilization than the limestone. Again, the variability observed in the data to date preclude drawing definite conclusions on the effect of temperature or residence time. Temperature, as with the limestone appears to have a minimal effect over the range studied and the majority of the sulfation appears to have occurred within 0.25 - 0.4 seconds. This is consistent with the surface areas generated during calcination of $Ca(OH)_2$ (Figure 7b); all the surface areas were in the range of 10 to 15 m^2/gm.

More interesting results were obtained with the pressure hydrated dolomitic lime as shown in Figure 10. This material exhibited utilizations on the order of 20 to 25 percent when the reactor was operated at 1600-1800°F with sulfation occurring within a residence time of 0.3 seconds. When the temperature was increased to 2000°F, the utilization increased to the range of 50-55 percent for residence times between 0.25 and 0.35 seconds. Further tests are in progress to extend this range of residence times at this higher temperature condition. These trends with residence times and temperature are consistent with pilot scale work reported in another paper in this symposium (Ref. 7).

A question still remains as to what limits high utilization of these calcium based sorbents; kinetics and reactive surface area, pore plugging, or solid diffusion. To provide some insight into the limiting mechanism the surface area of the sulfated pressure hydrated dolomitic lime was determined and is plotted as a function of utilization in Figure 11. During the sulfation process the surface area decreases from a calcine surface area of 25-37 m^2/gm to under 10 m^2/gm as the utilization exceeds 50 percent. If all of the CaO surface area consisted of grains of a uniform diameter and each grain sulfated uniformly, the change in surface area should follow the shaded band in Figure 11. The change in surface area is significantly greater, suggesting either: (1) the concept of uniform sulfation of a grain is not correct and that visualizing the process as sulfation of a pore where a larger change in surface area per unit of sulfation occurs is more correct, or (2) pore plugging limits access to active surface, or (3) the sulfated layers from adjacent grains merge to decrease access to reactive surface.

SUMMARY

The following summary points can be made from the bench sacle results to date:

- Limestone calcination rates at temperatures over 1800°F are relatively fast with 80 percent calcination occurring within a residence time of 0.3 seconds for the Marianna limestone, and 0.5 seconds for the St. Genevieve limestone.

- Calcination rates are a function of the initial surface area of the limestone.

- Limestone calcination rates measured in this study were slower than rates determined under conditions where kinetics dominates (Ref. 6) suggesting a CO_2 diffusion limitation within the particle.

- Surface area of the limestone calcine increases during calcination; for the Marianna limestone the surface area increased by a factor of three. Calcine surface area decreases as calcination becomes complete.

- Calcination rates of the hydrated materials are more rapid than the carbonates, with the majority of the calcination occurring in less than 0.2 seconds.

- During calcination of the calcium hydroxide the calcine surface area was less than the initial surface area at residence times greater than 0.2 seconds; while the calcine surface area of the pressure hydrated dolomitic lime increased with residence time and temperature.

- Sulfation of the limestones and $Ca(OH)_2$ was relatively insensitive to temperature and residence times with utilizations in the range of 12-20 percent and 15-27 percent respectively. The majority of the sulfation occured within a residence time of 0.25 seconds.

- Utilization of the pressure hydrated dolomitic lime increased as the temperature increased from 1800°F to 2000°F. Utilization at 2000°F was on the order of 50-55 percent.

ACKNOWLEDGMENTS

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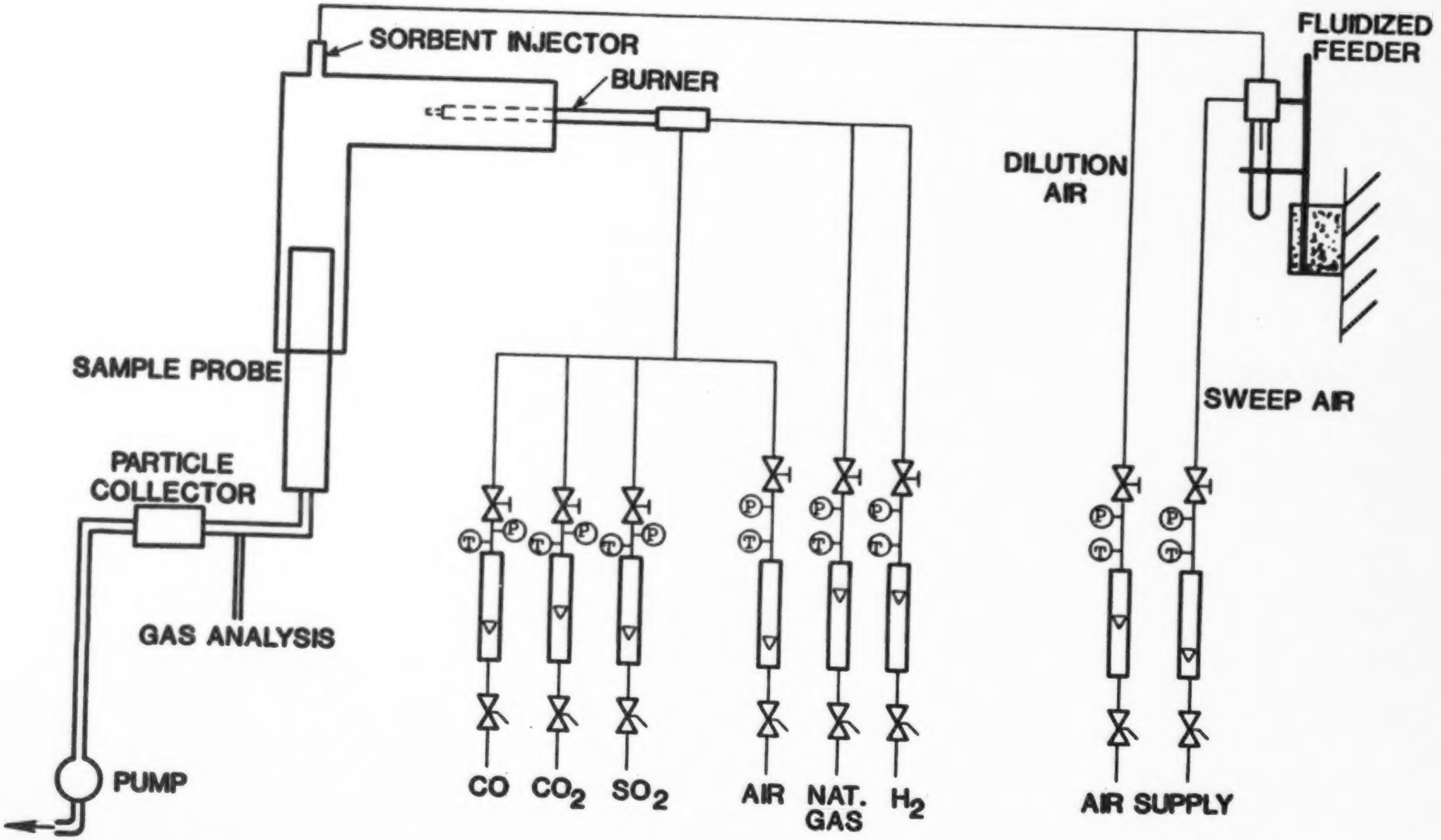
SORBENT INJECTOR
BURNER
FLUIDIZED FEEDER
DILUTION AIR
SWEEP AIR
SAMPLE PROBE
PARTICLE COLLECTOR
GAS ANALYSIS
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CO
CO_2
SO_2
AIR
NAT. GAS
H_2
AIR SUPPLY

Figure 1. Flow Reactor System

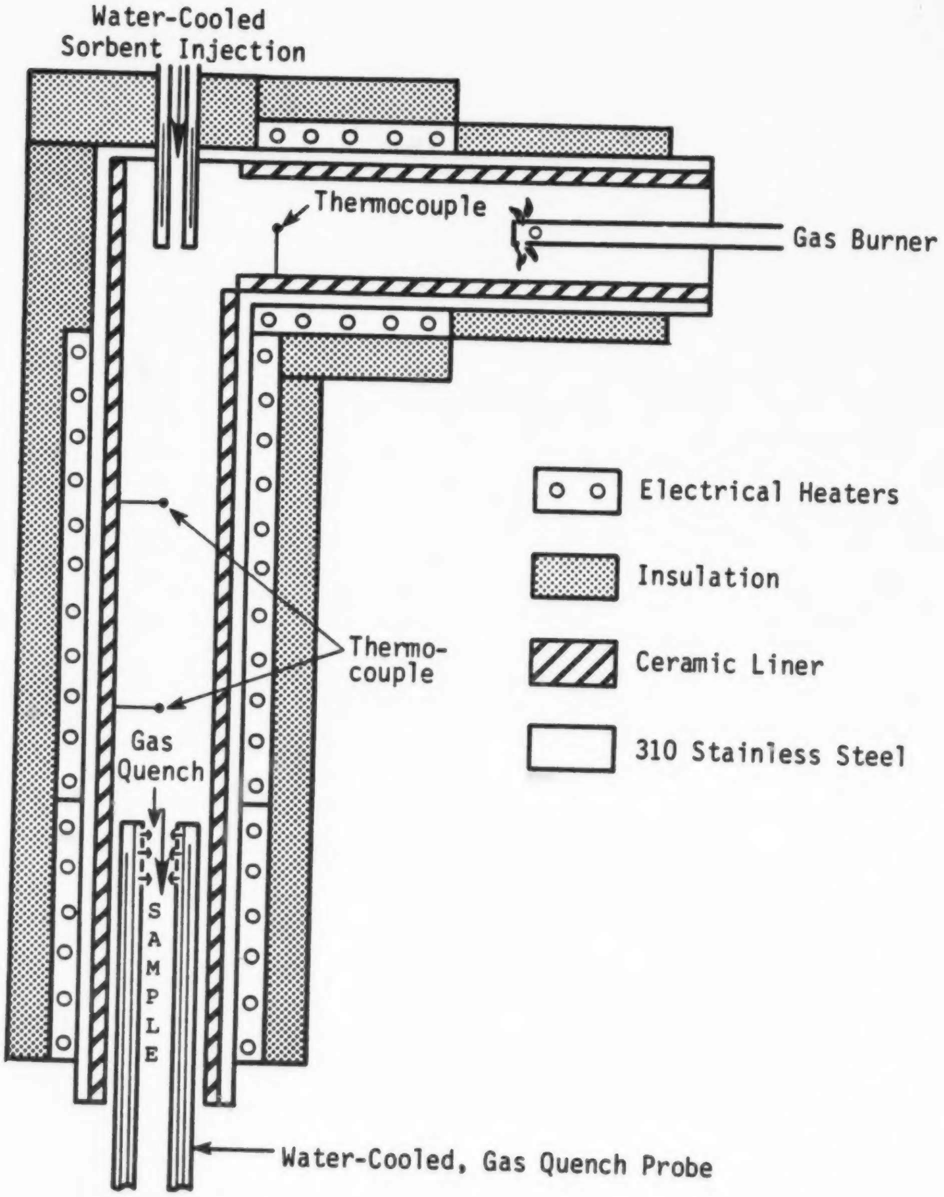
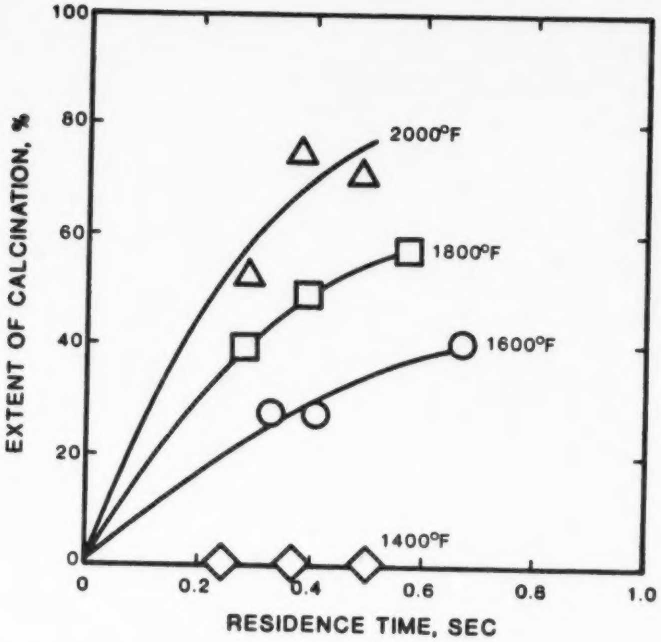
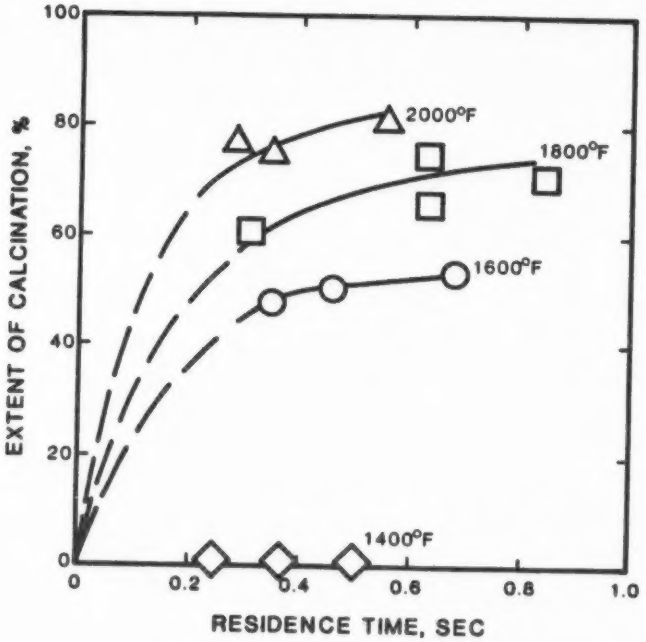

Water-Cooled
Sorbent Injection
Thermocouple
Gas Burner
Electrical Heaters
Insulation
Ceramic Liner
310 Stainless Steel
Thermo-
couple
Gas
Quench
SAMPLE
Water-Cooled, Gas Quench Probe

Figure 2. Flow Reactor Details



(a) St. Genevieve Limestone



(b) Marianna Limestone

Figure 3. Calcination of Limestone

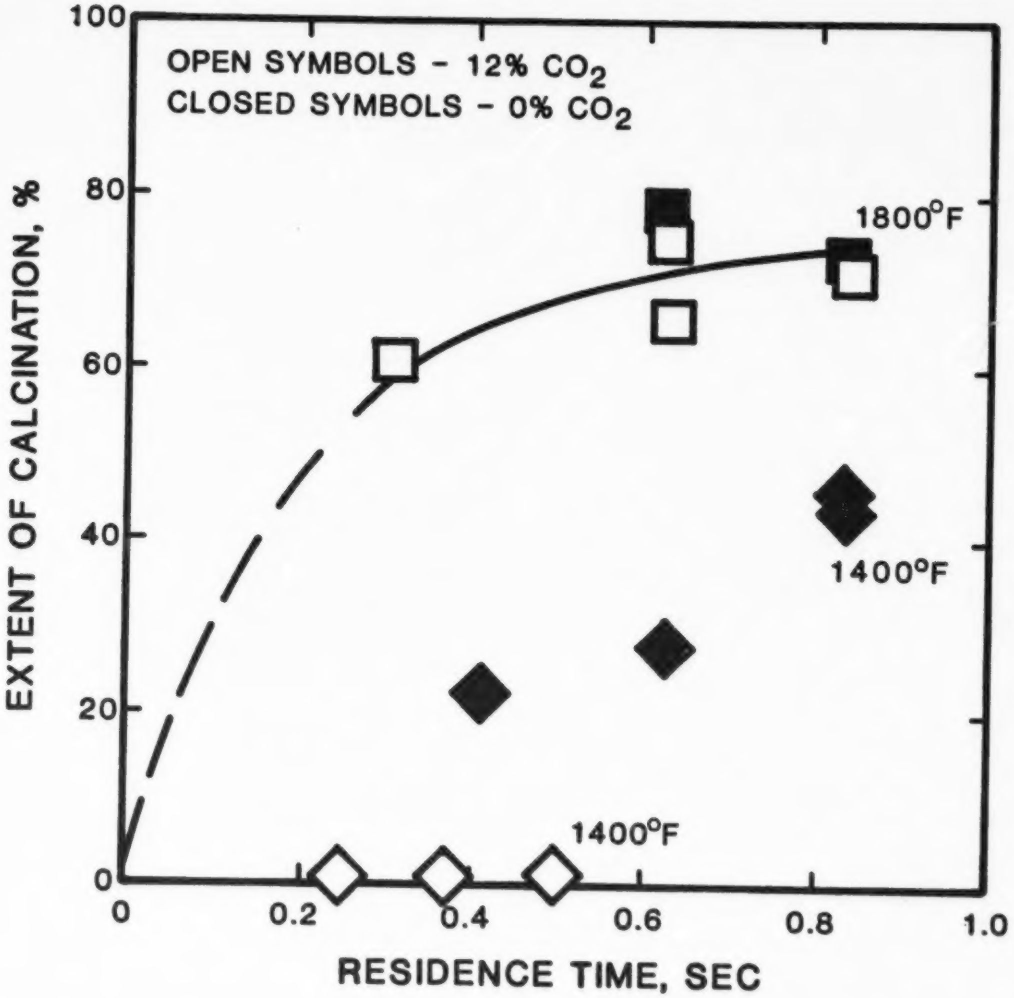


Figure 4. Effect of Gas Composition on Calcination of Marianna Limestone

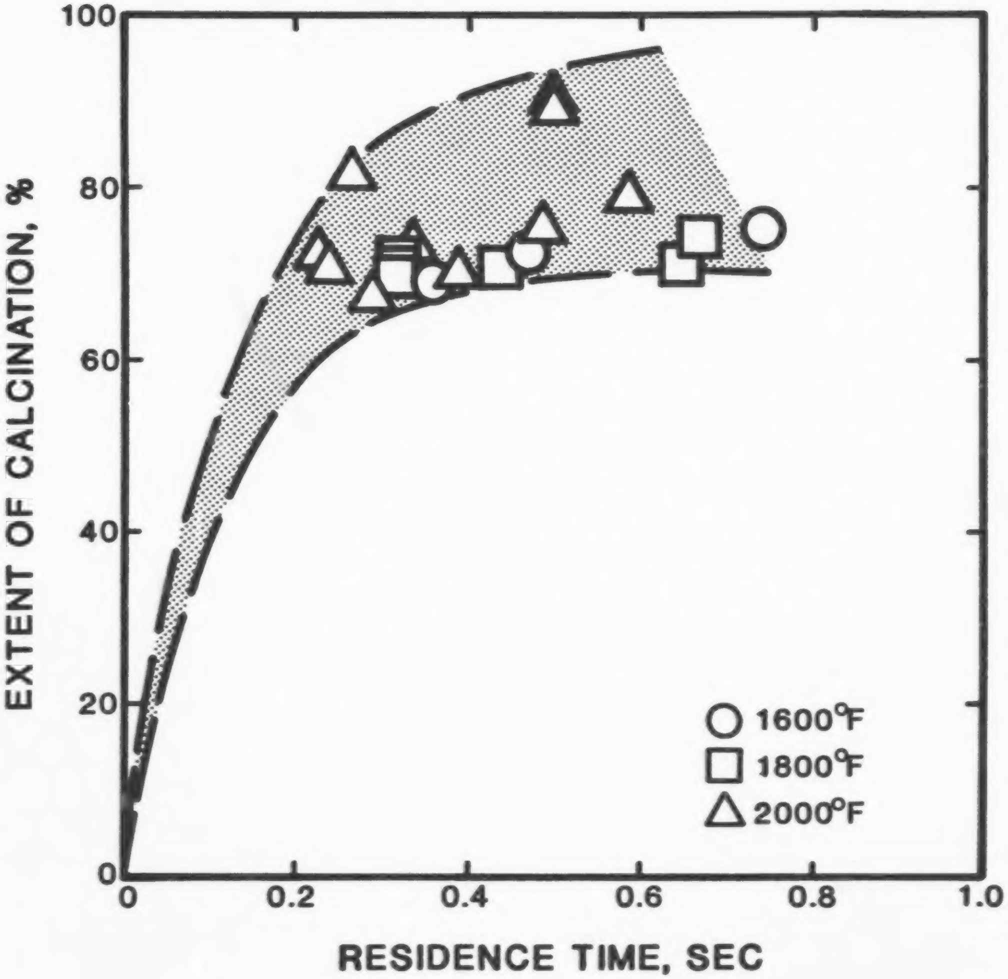


Figure 5. Calcination of Calcium Hydroxide

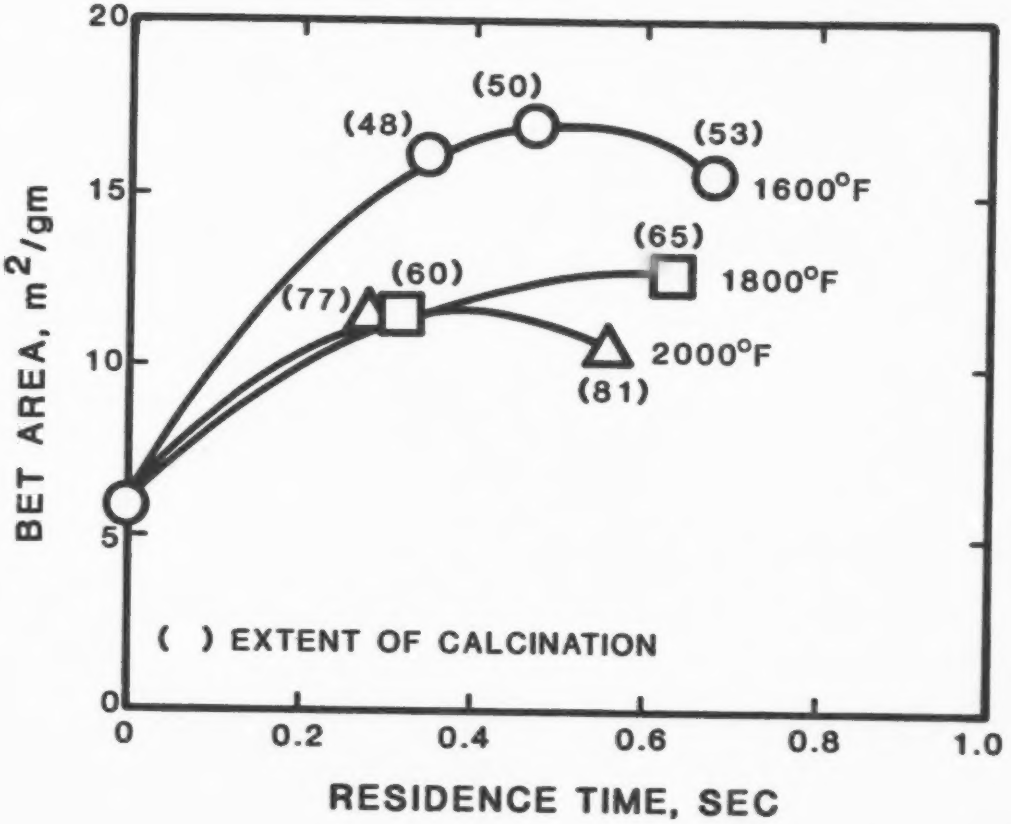
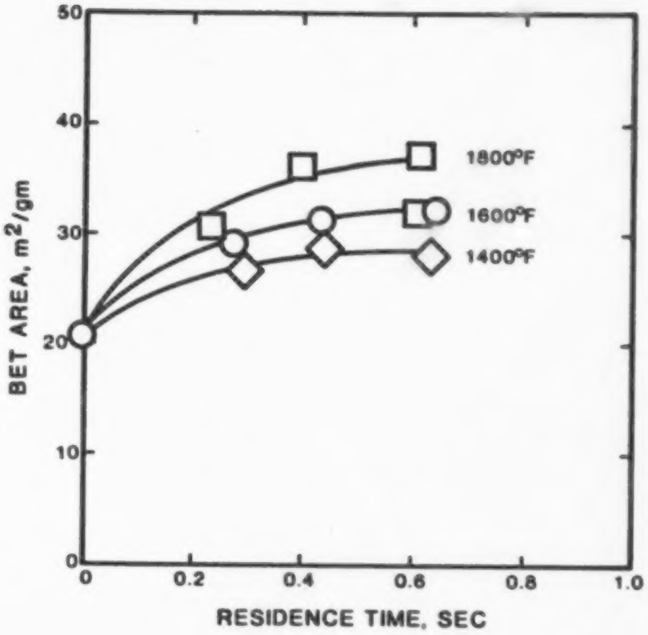
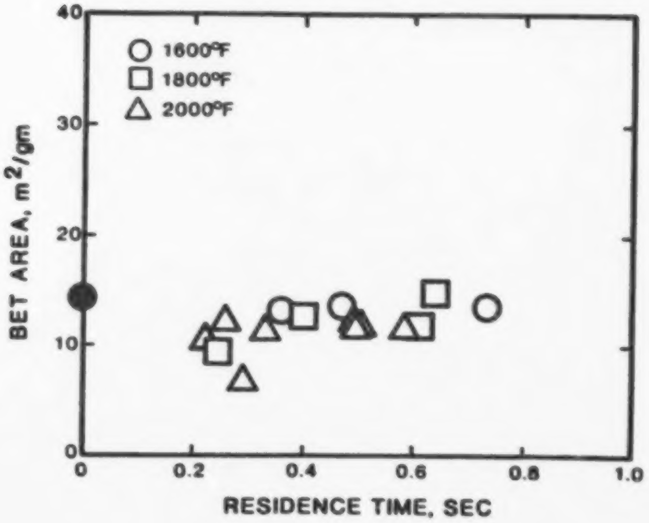


Figure 6. Evolution of Surface Area during Calcination of Marianna Limestone

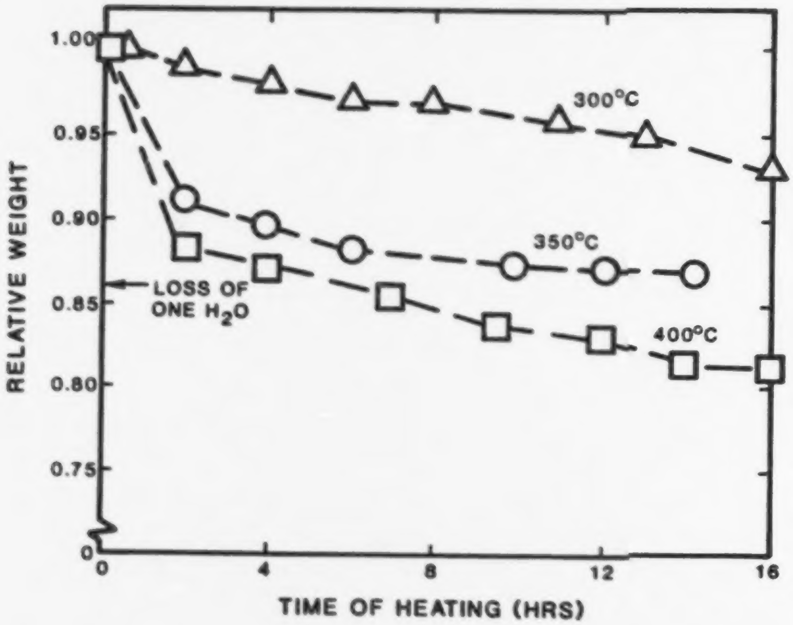


(a) Pressure Hydrated Dolomitic Lime

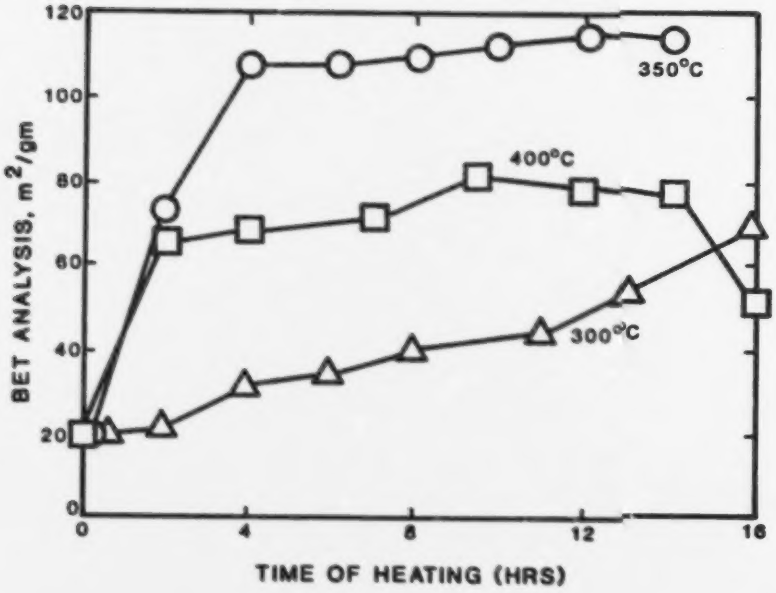


(b) Calcium Hydroxide

Figure 7. Evolution of Surface Area during Calcination

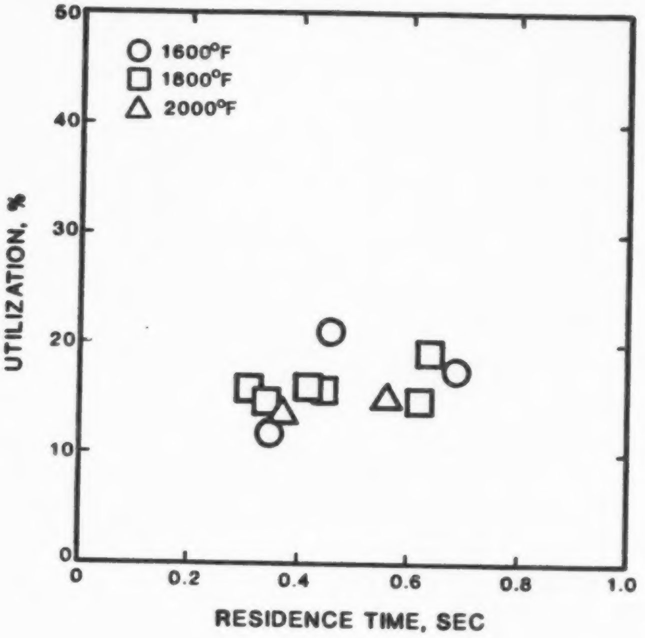


(a) Weight Loss

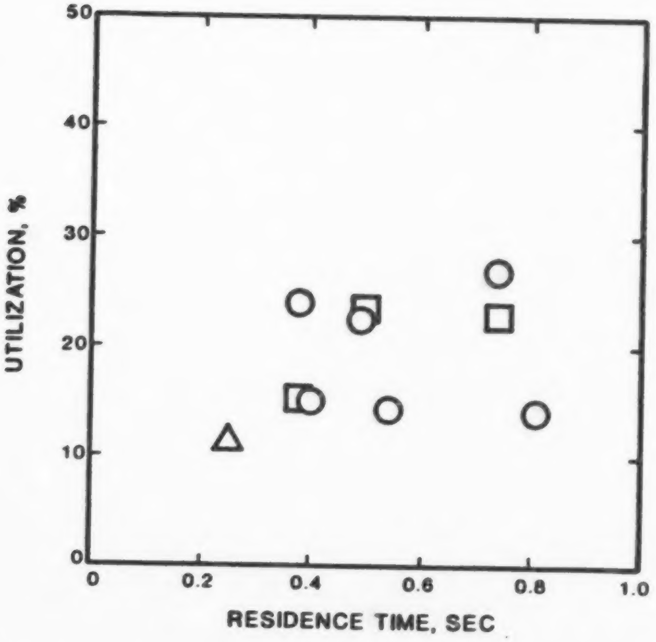


(b) Surface Area

Figure 8. Evolution of surface area upon heating pressure hydrated dolomitic lime.



(a) Marianna Limestone



(b) Calcium Hydroxide

Figure 9. Sulfation of Limestone and Calcium Hydroxide

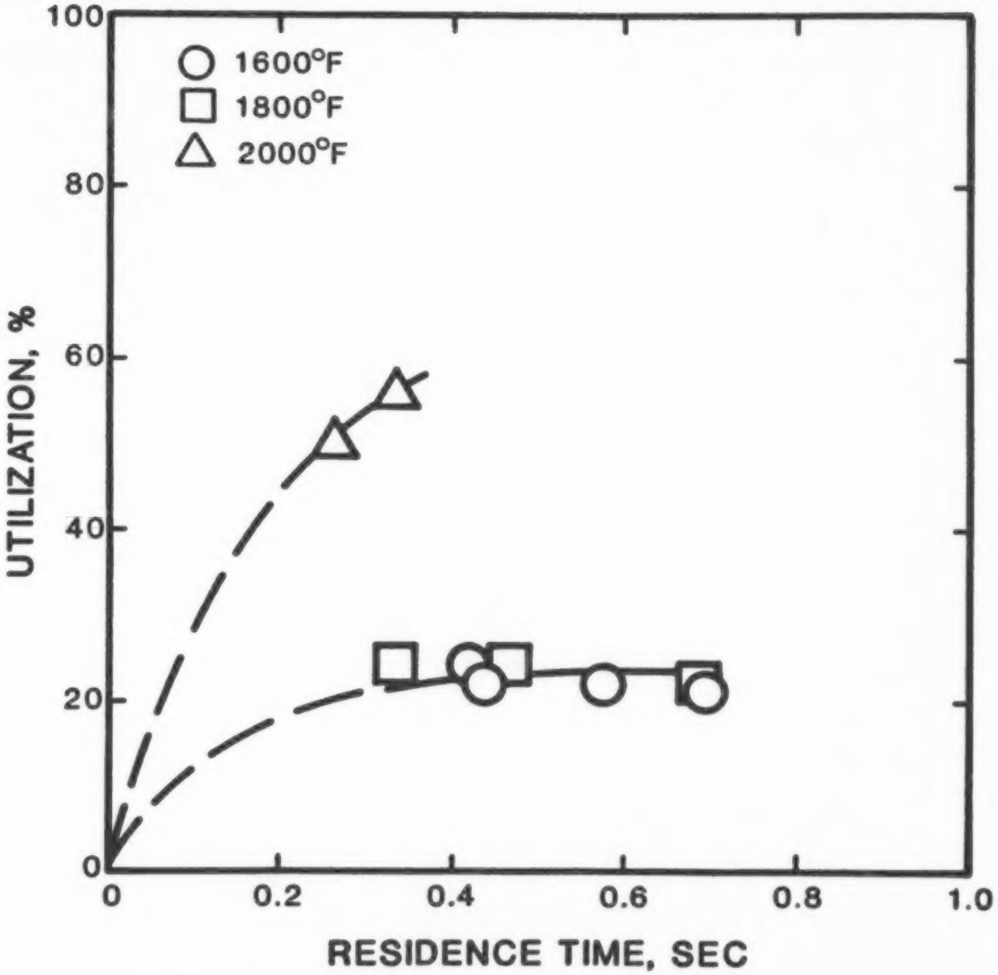


Figure 10. Sulfation of Pressure Hydrated Dolomitic Lime

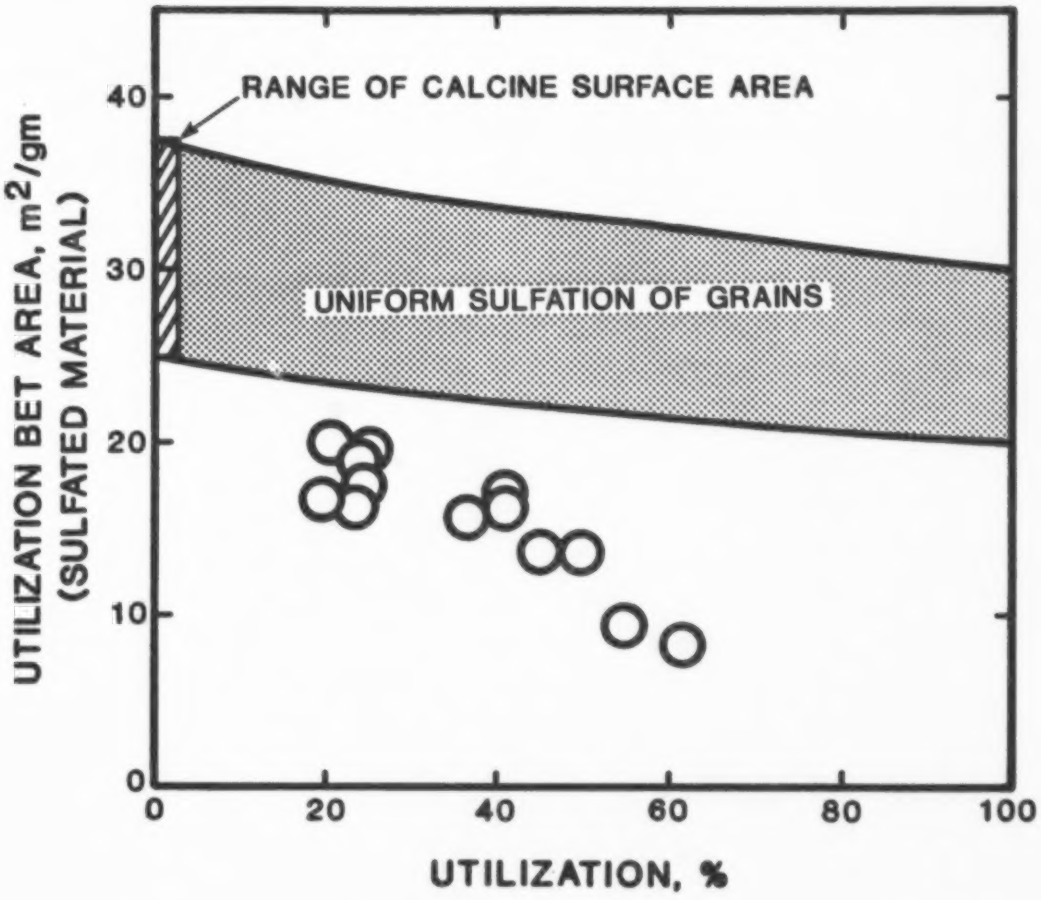


Figure 11. Change in surface area during sulfation of pressure hydrated dolomitic lime.

Table 1

SORBENT CHARACTERISTICS

	St. Genevieve Limestone $CaCO_3$	Marianna Limestone $CaCO_3$	Calcium Hydroxide $Ca(OH)_2$	Pressure Hydrated Dolomitic Lime $Ca(OH)_2$ $Mg(OH)_2$
CaO_2, wt%	53.1	50.1	72.2	43.1
Mg O, wt%	0.9	1.0	2.0	30.3
Particle size, MMD,)m	8.4	30	2.3	1.3
Density, gm/cm^3	2.71	2.70	2.24	2.30
Surface Area BET m^2/gm	1.7	6.3	14.3	19.6

CALCIUM-BASED SORBENTS FOR DRY INJECTION

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ABSTRACT

Dry injection technologies for SO_2 capture require that the mass mean diameter of the sorbent particle be relatively small, less than 20μ, to obtain removal rates high enough to make the process economically competitive with wet scrubbers. The least expensive method of producing fine sorbent particles is by hydrating lime. Typical commercial hydrates have a mass mean diameter less than 5μ. New studies of hydrate particles used in SO_2 capture show that the reactant layer is less than 1000 Å thick, the subject of this paper. These studies define the limiting mechanism for sorbent utilization, i.e. the conversion ratio of CaO to $CaSO_4$. Moreover, this understanding of the SO_2 adsorption process points to how hydration production methods might be modified to enhance SO_2 capture.

CHARACTERIZING PARTICLES

"Calcium-based sorbents" for all practical considerations means limestone or its derivative products: lime, essentially calcium oxide, CaO; and/or hydrate, $Ca(OH)_2$. There are also industrially precipitated calcium carbonates, $CaCO_3$, and natural ocean bed deposits of calcareous sands. For dry injection into boiler zones where the temperature exceeds 1000°C both the carbonate and hydrate formulations will calcine to the oxide, CaO. The SO_2 control reaction thus occurs with calcia, or lime, i.e., CaO, irrespective of the initial calcium composition. Much of the physical and chemical description of CaO is dependent upon its processing pathway, and some of those properties are critical to the adsorption of SO_2: specific surface area; mass mean diameter of the particles; and, chemical composition and physical chemistry of the particle surface. In order to ascertain what are desirable attributes of sorbent particles, it is necessary to understand how SO_2 is adsorbed onto CaO.

In a broad review of the existing data for SO_2 adsorption into lime, there are two quasi related trends which are obvious: the fractional conversion of CaO to $CaSO_4$ is inversely related to particle size; and as the particle size decreases the specific surface area plays an increasing important role in SO_2 capture. Large particles, bigger than 30 or 40 microns, perform poorly in terms of SO_2 capture and are resistant to improvement by any means, e.g. time-temperature profile in an SO_2 laden gas, SO_2 concentration, and increasing the specific surface area of the sorbent.

Diffusion limitations of an unreacted core model suggest, and empirical data supports the idea, that SO_2 capture is improved by using small particles with a high specific surface area. Thus the limit of Ca conversion is at least a combined function of particle morphology and geometry.

Powders that are produced by grinding and/or pulverizing may be reasonably well approximated in mathematical treatments by spheres or regular geometric solids with an aspect ratio (length:width:height) close to 1; powdered limestone and the derivative lime that is calcined from it are examples of such materials. Instruments that measure particle size for example assume that the particles have an aspect ratio close to 1 in the calculations used to determine size distribution. Such an assumption for hydrate particles has little correspondence to reality: the particles are often serpentine, highly irregular in shape and are commonly clustered into built-up forms; they may have aspect ratios as high as 50:1:0.1.

If the calculated surface area of a material (the surface area of spheres having diameters defined by the particle size distribution) is substantially less than the measured specific surface area then the conventional view is often that the particles must be porous. In the case of hydrate particles the measurement of particle size distribution by means of the usual commercially available instruments may be somewhat misleading in that the instruments do not account for irregular shapes with significant length to diameter ratios; i.e., the very nature of hydrate. An accurate characterization of hydrate requires SEM micrographs, and often TEM micrographs and surface analysis with SIMS in addition to particle size and BET specific surface area.

In the pursuit of small particles with high specific surface areas, it is necessary to constantly keep in mind that the entire dry sorbent injection technology is driven by economics: wet scrubbers using Mg enhanced lime perform extremely well: 99+% SO_2 removal at a stoichiometry of essentially 1, they are, however, expensive to install. The cost advantage that a dry injection system might have deteriorates rapidly as the unit cost of sorbent used to capture SO_2 increases. The quest thus is one of low cost, small particles with a high specific surface area, with emphasis on "low cost". Obtaining small particles, 100% less than 20μ, by grinding down rocks is not an attractive proposition, particularly in view of the fact that the typical commercial hydrate has an mmd of less than 10μ, usually around $2 < \text{mmd} < 4\mu$.

Producing calcines, i.e. CaO, from $CaCO_3$, with a very high specific surface area is thwarted by some basic fundamental relationships: specific surface area of CaO from $CaCO_3$ is inversely related to both the temperature of calcination and the partial pressure of CO_2. Commercially produced lime has a specific surface area of about $1 m^2/g$, with a ratio of the total gas flow to lime produced being about 3:1, 3kg total gas flow for 1kg of lime from a kiln. The throughput or product flux of a kiln system is typically on the order of 0.1 T/hr. per sq.ft. of cross-sectional area of 1 metric ton/hr. per m^2. Moreover, the kiln atmosphere is the combustion gases of the coal used for fuel. Current laboratory experiments that have produced high specific surface area calcines (40 to 60 m^2/g) use dry N_2 sweep gas at a gas to lime ratio of 20 or more with a product flux of less than 1% of a commercial kiln. The reason for the low material density is so that the CO_2 evolving during the calcination of one particle doesn't provide a partial pressure of CO_2 for adjacent particles (a commercial lime kiln runs about 30-35% CO_2 atmosphere). About one-third of the unit cost of producing lime is for capital equipment: equipment costs divided by output; if the equipment cost of a special kiln for high specific area lime were comparable to existing kilns but the throughput were only one-tenth that of conventional kilns (this allows for a tenfold improvement from present laboratory experiments due to economics of scale and learning more about the design requirements) the resulting lime would have an FOB price around \$160-180, vs. \$40-50 for commercial lime. Experiments that have produced calcines with 100 m^2/g or more specific surface area have used conditions so exotic (combinations of very small particles, approaching a 1μ mmd, and/or very high sweep gas rates) that the CaO cost would be in the range of 20¢ to \$1 per ounce, too high by more than a factor of 100 to be practical.

Prospects for significant step function increases in the specific surface area of lime from commercial kilns and/or minimizing the exotic conditions now employed in experimental work that yields high specific surface area calcines are the proverbial two: slim and none. Improvements in any technology tend to trail off with time, the learning curve gets flatter and flatter as a field of pursuit matures. At one end of the spectrum is computers, their capacity per dollar is still doubling about every two years with little evidence yet of it trailing off, but the industry is hardly 30 years old; conversely, the lime industry is known to be at least 10,000 years old with kilns discovered in archeological sites in Africa dating back 25,000 to 40,000 years. Today an improvement of just 10% in the cost of producing lime or the output of a plant would be considered close to astonishing. Hopes for finding 10-fold or 100-fold step increases in specific surface area without commensurate increases in cost are simply not very realistic. There is, however, much to be done with hydrate, a material, and its methods of production, that have escaped significant scientific inquiry for most of this century.

The reaction of SO_2 with secondary calcia (CaO derived by calcining hydrate) is a surface or near surface phenomenea. Analysis with SIMS and ISS of hydrate injected into combustors with SO_2 present shows that the conversion of CaO to $CaSO_4$ does not significantly intrude beyond 500 to 1000 Å into the particles, in fact in most cases there is little sulfate more than 500 Å deep.

Theoretical treatment of SO_2 being adsorbed into a secondary calcia particle is made difficult by the nature of the hydrate particle itself. Conventional models that deal with a reactant layer on a shrinking core assume that the surface or near surface material is not significantly different than the bulk substance in terms of defects, site energy, etc. and that the shape is a regular geometric solid, i.e. a sphere or close to it. In reality the reaction layer of a particle where SO_2 combines with CaO is almost entirely defined by defects, edges, surface chemistry, and the shape is anything but regular.

A combination of information from scanning electron microscopy (SEM), transmission electron microscopy (TEM), both with energy dispersive spectroscopy (EDS) capability; and SIMS makes it possible to piece together an image of how SO_2 and CaO react. The particle surface, which is less than pure CaO, encounters SO_2 and O_2, it begins to form $CaSO_4$, among other compounds, probably initially as a monolayer but growing in thickness to become an amorphous film, then microcrystalline and finally an increasingly thick and more completely crystalline coating over an unreacted core of CaO. Since $CaSO_4$ is a salt on an oxide it forms a complete, smooth, relatively impervious coating (thus reducing the free energy of the oxide surface); the other surface compounds are commonly Na_2SO_4, $CaCl_2$, $CaCO_3$, Na_2CO_3, and Na_2O.

Once the surface develops into a well defined $CaSO_4$ layer, further CaO utilization is limited by a double diffusion: SO_2 and O_2 through the $CaSO_4$ layer; and the diffusion of CaO and $CaSO_4$ with each other.

Several attempts have been made to alter the basic limitation of CaO conversion to $CaSO_4$ through the use of additives which combine with the $CaSO_4$ layer and substrate CaO to significantly alter the rate of CaO diffusion into the modified $CaSO_4$ layer. There are any number of compounds that will function to increase the diffusion of CaO in $CaSO_4$, ones with sodium are perhaps the most obvious. This changes the binary $CaO/CaSO_4$ reactant layer to at least a quaternary system of $CaO \cdot CaSO_4$ - Na_2SO_4 - Na_2O. In reality the coal combustion flue gases contain chlorine as well, and the sorbent surface contains some NaCl as an impurity so that the overall system phase diagrams have a considerable liquidous and/or two phase liquid/solid regions. The surface system is also more complex than quaternary: $CaSO_4$, $CaCl_2$, Na_2CO_3, KCl, $CaCO_3$.

The mechanisms for mixing additives and sorbents are three:

(A) The additive and sorbent are mixed and injected into the boiler where the additive vaporizes, then condenses out of the vapor state onto the sorbent particle, but also on the fly ash, boiler walls, tubes, etc. Transfer of the additive to the sorbent surface is not very efficient; $NaHCO_3$ is in this category.

(B) The additive and sorbent are mixed and injected into the boiler where the additive melts and/or will form a solid-state compound with CaO. To be effective this requires that the sorbent and additive particles are small enough and mixed intimately enough that they cling together and/or collide in the boiler.

(C) The additive is applied to the surface of the sorbent particle prior to injection. This can be done by washing limestone with a solution of the additive or in the case of hydrate the additive can be included in the water used for hydration. If the additive is more soluble than $Ca(OH)_2$ then with a carefully designed hydrator the additive will be largely contained on the surface of the hydrate particle.

The size, shape, surface morphology and chemistry of hydrate particles are determined by a combination of:

(A) Reaction rate of the water and lime.

(B) The time lapse to evaporate any excess water.

(C) Additives in the water and impurities in the original lime.

Hydration kinetics, i.e. crystallization of $Ca(OH)_2$ from $CaO + H_2O$, defines the basic particle morphology. There seems to be almost a basic unit structure of hydrate when lime and water are mixed and there is any appreciable delay (more than 1 or 2 seconds) before the heat of reaction vaporizes the excess moisture: an obloid shape, 200 to 1000 Å long with an aspect ratio of about 2, i.e. its diameter is roughly half its length. Liquid-mixed hydrate particles up to centimeters in size when viewed in SEM micrographs all appear to be built-up collections of these same basic pieces.

The morphology of hydrate particles resulting from steam and lime, or a water spray (fog) striking an excess of CaO yields particles with vastly different surface structures than the liquid mixed particles have. There is yet another variable, additives, which alters the particle surface even more.

The demonstrated efficacy of additives used with hydrates and their limited penetration into the reacted sorbent particles emphasizes the fact that the surface characteristics and morphology of the sorbent particle are the critical determinants in capturing SO_2. While it is essential that the sorbent particles are small, it is probably critical that the particles be small (1μ or less) in only one dimension, not all 3.

There is also the prospect that for boiler injection some combined oxide forms may have a higher affinity for sulfur dioxide than CaO with just a modified surface. Work in the steel industry on ladle metallurgy for desulfurizing specialty steels would suggest certain combinations of lime, alumina and silicates might be a promising avenue of investigation. The "designed formula lime" can be made by briquetting combinations of limestone, hydrate and/or hydrate with additives, bauxite, etc. which is then fired in a commercial lime kiln; the product is hydrated as the most economical method of obtaining very fine particles, and then injected into the boiler where the hydrate reverts to the oxide. To date only a few formulations have been produced by this method and are yet to be tested in a combustor.

The possible combinations of compounds, and their concentrations in a designed lime product, in addition to a variety of hydration methods yields a myriad of potential sorbents to evaluate. In view of the fact that neither the unreacted core model (for roughly spherical particles), nor a porous solid model are realistic representations of hydrates and their derivative oxide forms it may seem that there is little alternative but to matrix through the list of possible sorbents that could be manufactured. However, it seems much more efficient to attempt to model the system: computer graphics, particularly fractals, along with descriptions of behavior from physics, chemistry and thermodynamics have the potential of creating a technique for evaluating the sequence of "designed lime-hydration-dehydration/sulfation."

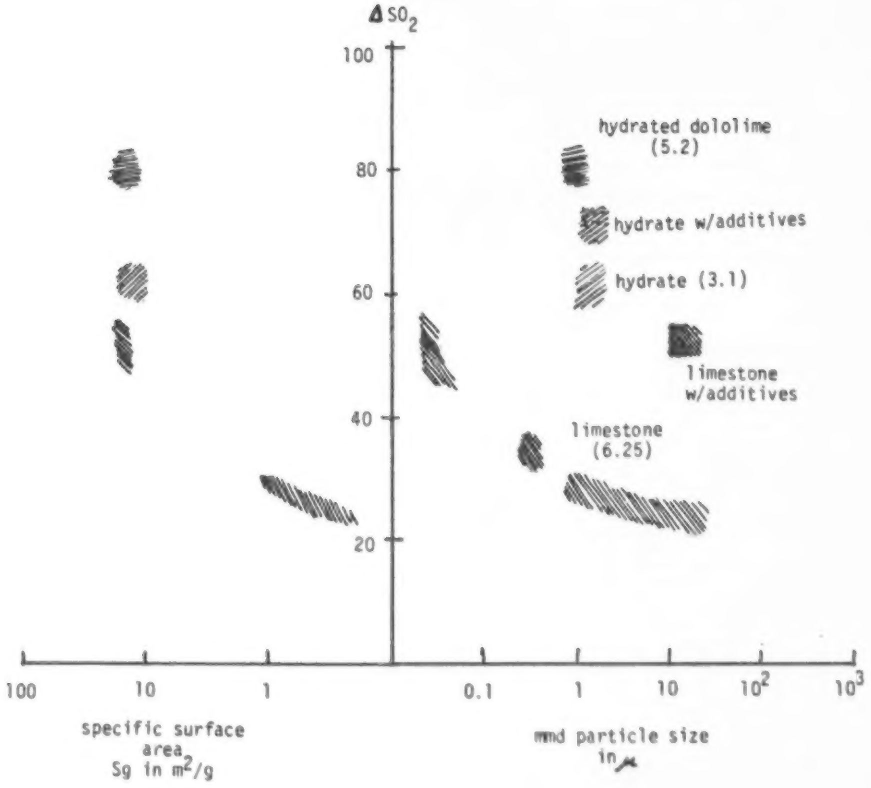


Figure 1. Relationship of measured particle size, BET specific surface and sulfur dioxide removal in a combustor. The sorbent to captured sulfur dioxide ratios are on a weight basis.

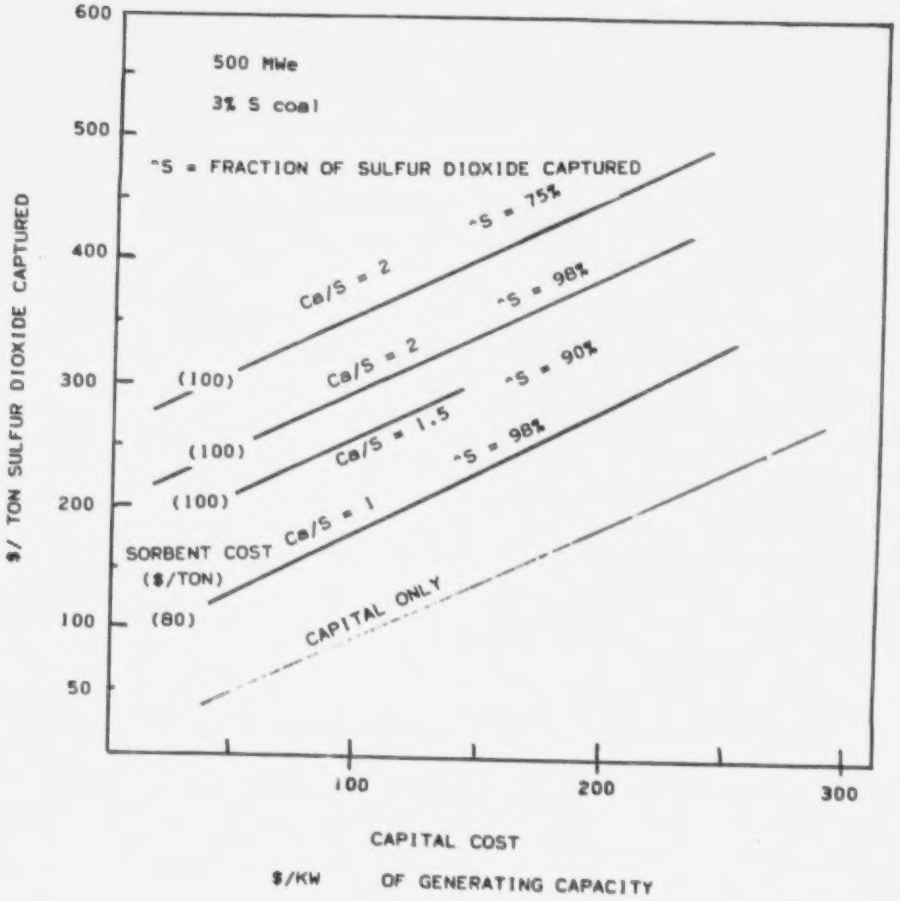
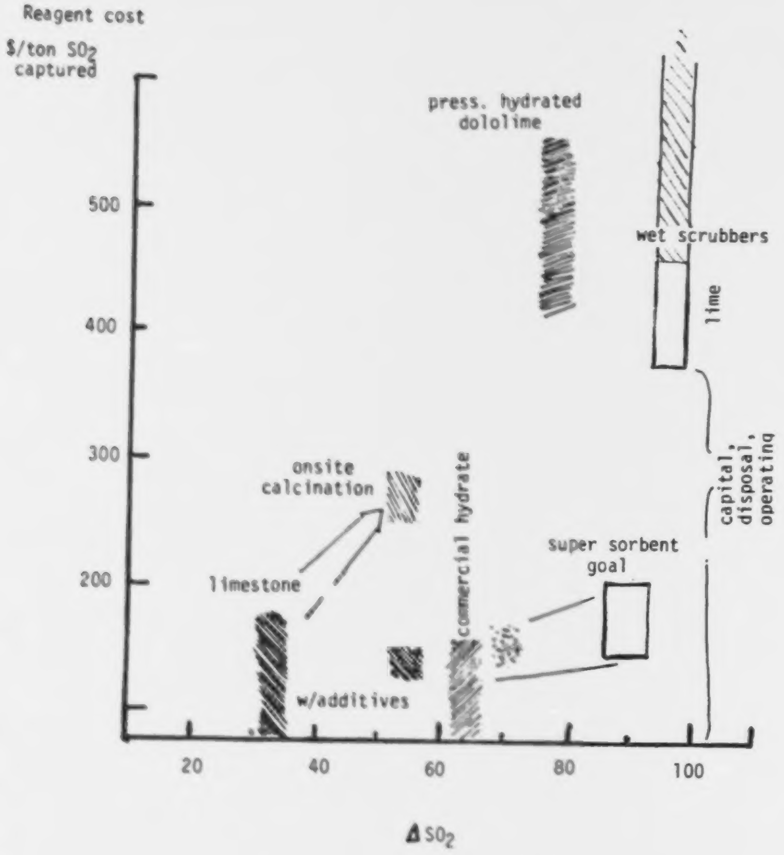


Figure 2. Effect of reagent cost added to capital cost (15-year depreciation) and its effect on cost of captured SO_2. To offer significant advantages over wet scrubbers, a dry injection technology must have an installation cost half that of wet scrubbers and use a reagent that costs less than $150 per ton.



	FOB Sorbent $/Ton	Transportation $/Ton Sorbent	Onsite Processing Cost $/Ton Sorbent	Sorbent Cost at Utility	Reagent Cost $/Ton SO_2 Capture
CaO	50	20	8 hydr.	78	241.8
$Ca(OH)_2$	75	20		95	294.5
$CaCO_3$	5	20	18 grinding +55 onsite calcine	43 $CaCO_3$ /41 CaO	268.8 373.5
$[Ca(OH)_2 + Mg(OH)_2]$	85	20		105	541.8
	100			125	645

Figure 3. Combining the demonstrated performance of sorbents (Figure 1) with their calculated cost gives the reagent cost to capture a ton of SO_2. Total costs for wet scrubbers are included for comparison, as well as the technical/economic goal of the current research work (EPA funded contract) to find a "super sorbent" lime or lime product.

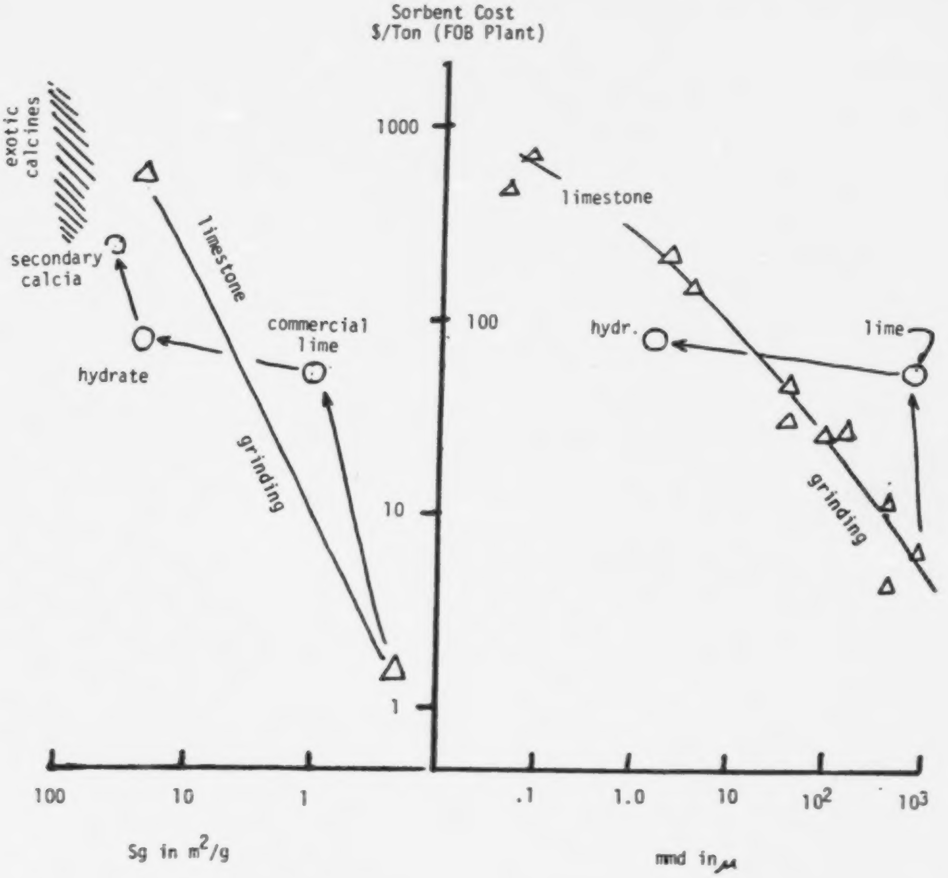


Figure 4. Calculated costs of obtaining small particles with high specific surface areas. Hydrated lime is a notable anomoly in the system, yielding small particles, reasonably large specific area at a significantly lower per ton cost than any other pathway.

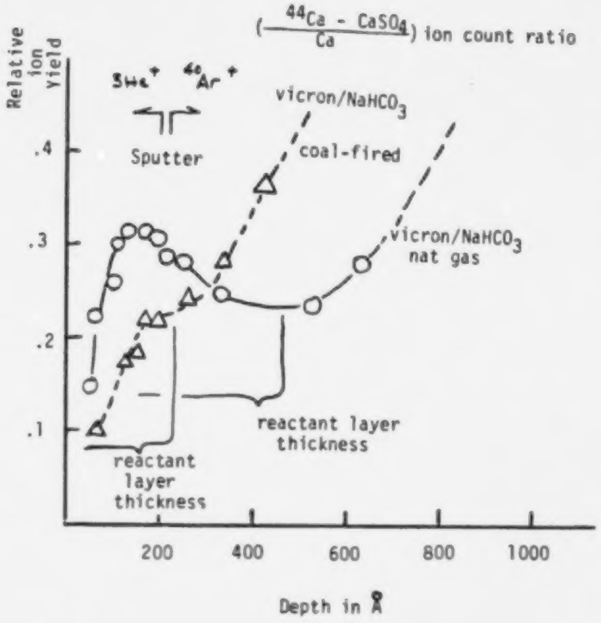


Figure 5. Depth profile of reacted sorbent particles showing sulfate reactant layer concentration and thickness. Data was taken with SIMS-ISS system (Advanced R&D, St. Paul, Minn.) and treated mathematically after viewing SEM micrographs of sorbent particles (before and after ion milling) to calculate an apparent reactant layer depth.

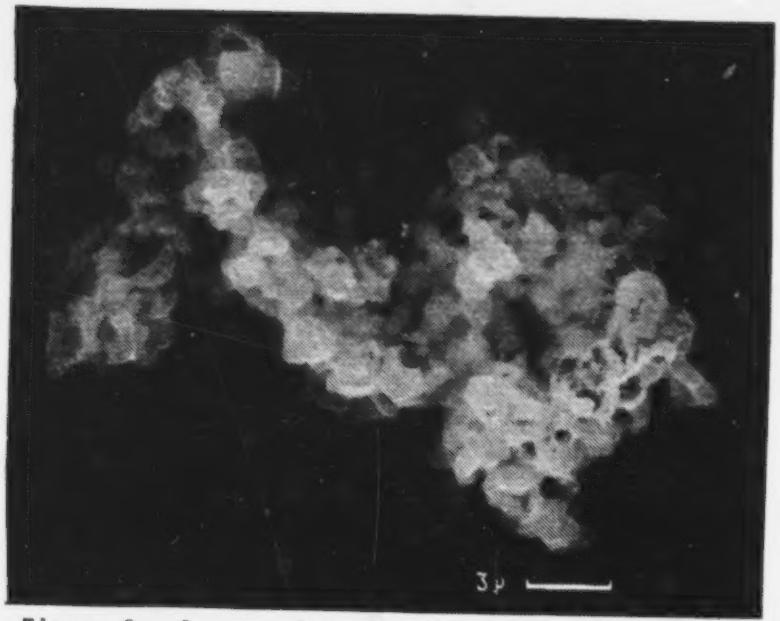


Figure 6. Common view of hydrate particle from a commercially produced hydrate product with an mmd of 2.5 microns and a specific surface area that averages 19 m²/g.

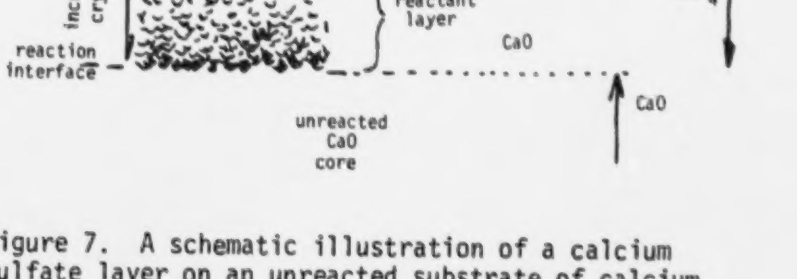
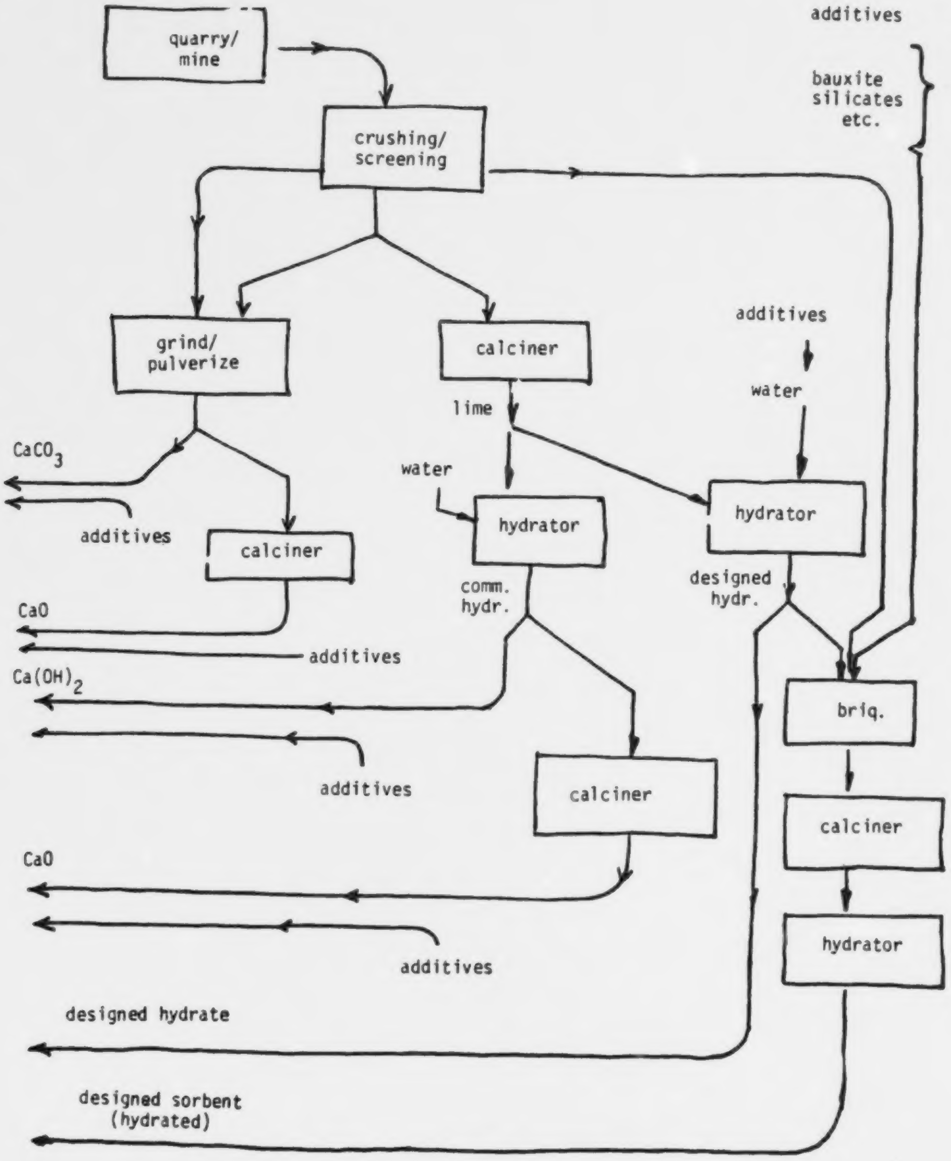

H_2O
CO_2
O_2
SO_2
$CaSO_4$
increasing crystallinity
surface
reactant layer
$CaSO_4$
CaO
reaction interface
unreacted CaO core
CaO

Figure 7. A schematic illustration of a calcium sulfate layer on an unreacted substrate of calcium oxide.



additives
quarry/ mine
bauxite silicates etc.
crushing/ screening
additives
grind/ pulverize
calciner
water
lime
CaCO$_3$
water
hydrator
hydrator
additives
calciner
comm. hydr.
designed hydr.
CaO
additives
Ca(OH)$_2$
briq.
additives
calciner
calciner
CaO
hydrator
additives
designed hydrate
designed sorbent (hydrated)

Figure 8

SESSION II (PART 2): FUNDAMENTAL RESEARCH

Chairman, Dennis Drehmel, EPA, IERL/RTP

LABORATORY-SCALE PRODUCTION AND CHARACTERIZATION OF HIGH SURFACE AREA SORBENTS

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ABSTRACT

The objectives of the research described are to produce high surface area sorbents in an apparatus amenable to scale-up, and to determine those characteristics in the raw carbonates which correlate to the development of high surface areas in the calcined product. Thus far, limestones crushed to minus 600 μm have been calcined to produce maximum surface areas of from 40 to 58 m^2/g in a laboratory-scale fluidized bed reactor with a pulsed air flow. A dolomite similarly treated has produced a surface area of 74 m^2/g.

Particle size and elemental analyses of the raw stones have been performed, and a significant negative correlation between maximum surface area development and iron content has been noted. No correlation between surface area development and petrographic properties has yet been demonstrated.

INTRODUCTION

The U.S. Environmental Protection Agency is developing the limestone-injection multistage burner (LIMB) process as a cost effective means of achieving the simultaneous reduction of SO_2 and NO_x emissions from coal-fired boilers. As originally envisioned, the process was to control NO_x by staged combustion and SO_2 by injection of limestone with the coal. It was expected that the limestone would calcine to CaO in the higher temperature zone of the boiler and combine with SO_2 at lower temperatures downstream. Subsequent experimental evidence suggests, however, that optimal sulfur capture may not occur due to imperfect calcination of the limestone and/or to an interaction between the sorbent and mineral matter in the coal. Additionally, experimental evidence on sulfation kinetics shows that SO_2 capture increases with the square of the sorbent surface area.(1) One effective alternative, therefore, appears to be calcination of limestone under more favorable conditions outside the boiler and injection of the resulting high surface area sorbent into the boiler at the upper portion of the sulfation temperature zone. In support of this approach to the LIMB process, the ongoing research described here has the following objectives: 1) to develop a laboratory-scale method, amenable to scale-up, of calcining limestones to high surface areas (35-45 m^2/g); 2) to determine the physical properties of the sorbents produced; and 3) to identify properties in the raw stone which correlate to the development of high surface areas in the calcined product.

CALCINATION

The investigation of methods to produce high surface area calcined sorbents progressed in two phases. The first phase consisted of a series of simple screening experiments to delineate the parameters thought to be important in governing maximum surface area. In this case the parameters were: 1) sorbent characteristics; 2) time; 3) temperature; 4) particle dispersion; 5) rate of flowing medium; and 6) composition of flowing medium. The second phase consisted of constructing and operating a fused quartz fluidized bed calcination unit to optimize surface area development.

Screening Studies

Samples for these experiments were drawn from a collection of 19 pulverized limestones and dolomites that were already on hand. Most of these stones consisted only of minus 44 μm material. Those that had a wider size range were screened at 44 μm to eliminate larger particle sizes. This was the only sample preparation performed on these materials.

To determine the degree to which sorbent characteristics govern surface area development, 5 g of each stone from the above collection was calcined at 850°C for 30 minutes in a quartz crucible. The atmosphere was still air. The resulting surface areas are recorded in Figure 1. The fact that dolomites as a group achieved higher surface areas than the limestones was expected, but it was somewhat surprising to note the inconsistent performance of chalks and marls. Research by Harvey, et al.(2) has suggested that these types of materials routinely produce high pore volumes and surface areas. The important result for this part of the screening effort is that, even among the limestones, the surface areas vary by a factor of nearly three. It appears that, aside from the distinction mentioned above between limestones and dolomites, sorbent characteristics play a more significant role in surface area development than was initially expected.

The next series of experiments focused on calcination conditions which might affect the maximum surface area produced. For this series two stones were selected from the above group: El Dorado limestone and dolomite 99, hereafter referred to as Kaiser dolomite. In each case the stones were calcined over a series of temperatures, comparing one other variable at a time.

In the first case only the means of dispersing the sample was varied. Of each stone, 2 g was calcined in a still air environment for 30 minutes at temperatures ranging from 750 to 900°C. The samples were placed in a quartz crucible for one run and dispersed on quartz wool for the other. As shown in Figure 2, both the limestone and dolomite achieved higher maximum surface areas, and achieved these maxima at lower temperatures when the sample was dispersed on wool. Dispersion therefore was assumed to play a positive role in surface area development.

In the second case 2 g of each stone was again calcined at temperatures from 700 to 850°C for 30 minutes. All samples were now suspended on quartz wool with a still air atmosphere used in one run and flowing air used in the other. Figure 3 shows that limestone achieves a higher maximum under the flowing regime and that dolomite is tending to achieve its maximum at a lower temperature. A flowing air regime, therefore, appeared to be beneficial in achieving higher surface area.

The results of the last screening experiment are shown in Figure 4. In this case 2 g of material dispersed on quartz wool was calcined for 30 minutes at temperatures from 700 to 850°C. In one run a flowing air regime was used, and in the second run flowing nitrogen was used. Both gases had been dried. The nitrogen atmosphere appears to have been beneficial in producing surface area in both stones; the dolomite achieved a higher maximum, and the limestone reached its maximum at a lower temperature.

The screening studies, despite their simplicity, held important implications for later work. It seemed clear that characteristics of the raw limestones could significantly affect surface area development and should be identified if possible. The importance of particle dispersion and a flowing regime suggested that fluidized bed calcination, already available commercially, might be adapted to the production of high surface area sorbents. The remainder of the research investigated these preliminary findings.

Fluidized Bed Studies

A new suite of samples was required for the fluidized bed experiments since the minus 44 µm material was too fine for fluidization and more costly for commercial production than a coarser size range. Discussions with lime industry representatives revealed that a minus 600 µm size fraction could be produced with state-of-the-art crushing and screening equipment. To obtain this size fraction for laboratory use, quantities of 2-5 cm stone were obtained from commercial lime or limestone suppliers, crushed in a Bico jaw crusher, ground in a Bico disc mill, and screened at 28 mesh (600 µm). Materials were then dried at 200°C for 8 hours and riffled and/or coned and quartered to 15 g sample size for calcination.

Figure 5 shows an exploded view and stock components of the fused quartz fluidized bed calciner designed to be operated in a Lindberg muffle furnace to temperatures of about 950°C. A constant flow of either air or nitrogen was supplied at 5 L/min, supplemented with a flow of 4 L/min, pulsed for 1 sec durations at 1 sec intervals to maintain fluidization.

Figure 6 shows the results of a suite of 15 g, minus 600 µm samples fluidized in nitrogen for 30 minutes at temperatures ranging from 700 to 850°C. This is assumed to be a base case in which conditions were optimized. All stones achieved their maxima in the 750 to 800°C range, with the single dolomite reaching a surface area of 69 m^2/g. The limestone maxima ranged from 40 to 50 m^2/g with an average of 45 m^2/g.

Figure 7 shows the results of a similar experiment, but with air instead of nitrogen as the fluidizing medium and with two additional stones from the screening experiments included for comparison. The results are both more erratic than the base case and somewhat unexpected. The screening experiments suggested that higher surface areas would be produced in a nitrogen atmosphere, but during fluidized calcination in air some surface areas decreased and others increased relative to the results achieved with nitrogen. The average of 44 m^2/g for the limestones is not significantly lower than the base case.

Figure 8 shows the results of reducing the fluidization time to 15 minutes in a nitrogen atmosphere. The data set must be regarded as incomplete since only the Clifton and Maysville stones were 100 percent calcined at 850°C. The remaining stones can be expected to gain additional surface area before reaching their maxima at 100 percent calcination, but even at this point the limestones had achieved an average surface area of 40 m^2/g.

CHARACTERIZATION

Calcined Sorbents

B.E.T. and TGA. The principal analytical techniques employed in this investigation for determining the sorbent properties of interest were the B.E.T. (Brunauer, Emmett, and Teller) method of surface area analysis and thermogravimetric analysis (TGA) for calculating the degree of calcincation. A Micromeritics Flow Sorb 2300 B.E.T. system was routinely used for single-point surface area analysis. The reader is referred to in-depth discussions on the nitrogen adsorption method of surface area analysis in Gregg and Sing (3) for details of the technique. TGA analyses for carbon dioxide (degree of calcination) were performed on a DuPont Series 99 thermogravimetric analyzer and used primarily as a check on the relative accuracy of the surface area measurements. The expected behavior is that surface area will increase with increasing calcination until 100 percent calcination is reached. From that point on, the sintering process will act to decrease surface area by collapsing the internal pore structure. Raw TGA and B.E.T. data for the fluidization experiments shown in Figures 6-8 are displayed in Table 1.

Another property of interest, and perhaps greater importance, is the distribution of surface area among the various pore sizes in the calcined sorbent. It has been assumed that much of the surface area in the high surface area materials is concentrated in the range of smaller pore diameters. If these pores are too small, however, they may quickly become inaccessible to the SO_2 molecules due to blockage by the sulfation production. It seems reasonable to speculate, therefore, that the "ideal" sorbent will eventually be defined by some optimal combination of surface area and pore size.

Surface area as a function of pore diameter can be determined either by mercury porosimetry or by multipoint analysis of desorption curves from the B.E.T. instrument. Again, the reader is referred to Gregg and Sing for details of this analysis. To determine the utility of these methods, a sample of Longview limestone calcined to about 50 m^2/g was analyzed on a Micromeritics Model 2100E and by a commercial laboratory using the mercury porosimetry technique. The results of these analyses are shown in Figures 9 and 10, respectively. Extreme care must be exercised in reading these plots since they cannot be interpreted as normal histograms. The bars are of unequal width because they are determined by the availability of data points on the horizontal axis, and extrapolation between these points is not appropriate. In Figure 9, for example, the wide 2 percent bar extending from 250 to 480 A* indicates that 2 percent of the total surface area is found within this total range of pore diameters; not that 2 percent is found within each category of the range as in a normal histogram.

The B.E.T. plot in Figure 9 suggests that the surface area is concentrated in the range of pore diameters from 80 to 140 A, while the porosimetry data in Figure 10 shows the range of highest concentration to be 180 to 260 Å. The utility of this type of analysis appears obvious, but the required accuracy for the purposes of this research and the available accuracy from the two techniques must be determined before it is extensively applied or firm conclusions drawn from results.

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* 10,000 A = 1 μm

SEM and TEM. In an effort to adequately visualize the calcined products and particularly to demonstrate the pore structure that was being created, a research grade Camscan Series 4 scanning electron microscope (SEM) with a maximum resolution of about 30 Å was employed. Reagent grade calcite samples were calcined to surface areas of from 12 to 28 m^2/g and viewed with the instrument. Figure 11 shows the results. Two important observations can be made from the photographs: 1) the external expression of the pore structure appears as an irregular series of fissures or cracks; and 2) there appears to be a directional nature to the pore development, perhaps governed by the orientation of twin planes within the crystal structure. If these observations prove to be applicable to other calcined limestones, they have interesting implications. The implication of the fissure-like nature of the pore structure may be that the assumption of cylindrical pores used in current sulfation models and in calculating derived values from B.E.T and porosimetry analyses is incorrect. The second observation leads to the interesting speculation that, if calcination (pore development) has a preferred direction, then so may sulfation. If this is true then stone crushed to a particle size of less than the crystal size may calcine to particles having a uniform directional orientation of both porosity and sulfation. This type of product may prove to be more effectively sulfated than one consisting of particles containing numerous randomly oriented crystals.

Figure 12 may lend support to the idea of a directional orientation to the porosity although its interpretation is not yet clear. It is a transmission electron micrograph (TEM) of one of the Maysville calcines. The crystals on the left are hydrated due to exposure, while those on the right appear to be lime. The dark areas may represent internal porosity preferentially oriented along the long axis of the crystals.

Raw Stone

Petrography. At present two samples of each of the raw stones have been thin-sectioned, stained to distinguish calcite from dolomite, and described petrographically. Large amounts of time have not been expended in point counting or statistically validating grain size. This may be warranted when the properties of particular interest are determined. No correlation has been observed thus far between petrographic characteristics and surface area development in the calcined product. Nomenclature used in classification is after Folk. (4)

Maysville stone (Figure 13) is a biolithite consisting of Tetradium coral fragments replaced primarily by untwinned sparry calcite ranging in crystal size up to 0.8 mm. Echinoid plates and spines, some partially replaced by chalcedony, are also abundant. Pelleted intraclasts add to the framework while micrite and pelleted micrite comprise the matrix. Dolomite rhombs are ubiquitous.

Longview limestone (Figure 14) is classified as an intrasparrudite or a pelsparite. It consists of alternating thin (1.5 to 3.0 mm) layers of pelleted micrite, pellets plus pelleted intraclasts, and intraclasts only, depending on the degree of sorting. Spaces between clasts are filled with twinned sparry calcite up to 1.0 mm in crystal size. No fossils are present.

Clifton stone (Figure 15) is a biomicrudite consisting largely of Rudistid mollusc shell fragments. The matrix consists of micrite and some shell hash. Generally untwinned sparry calcite up to 0.7 mm in crystal size is replacing some of the shell material as well as the matrix. The stone is extremely porous with as much as 15-20 percent open voids.

Round Rock limestone (Figure 16) shows two distinct lithologies. One is a biopelmicrite with a mollusc shell fragment framework. Interstices are filled with nearly equal portions of pelleted micrite and coarse (up to 1.00 mm) untwinned spar. The other is approximately half fossiliferous intrasparite and half fossiliferous intramicrite. Foraminifera are abundant with some echinoid fragments. Grains are generally rounded.

Genstar dolomite (Figure 17) also consists of two markedly different lithologies. The first one consists only of intergrown crystals up to 0.1 mm with all sedimentary features apparently eradicated by dolomitization. The second lithology is a dolomitized pelmicrite with alternating layers of micrite and large pellets (0.4 mm) in a micrite matrix. Some sparry material is found in pelleted layers and as crack filling. Ostracod and bryozoan fragments are present.

Particle Size. Analyses of particle size distributions in the minus 600 μm material used for the fluidized bed experiments were performed using an Allen-Bradley Sonic Siever and are presented in Table 2. Figure 18 shows a scatterplot of the median particle diameters versus the maximum surface areas achieved in both air and in nitrogen. No significant correlation is found using this limited amount of data although there is an indication that coarser sized material tends to develop lower surface areas. It would be expected that, for a given set of calcination conditions, an optimal particle size exists. Correlations will be sought when additional data are available.

Elemental Analysis. Elemental contents of the minus 600 μm materials were determined using x-ray fluorescence and are presented in Table 3. Figure 19 shows a scatterplot of the maximum surface areas achieved in air and in nitrogen versus iron content. A significant negative correlation is found with iron, and this is the only element that produced a significant correlation. The interpretation is not entirely clear in this case since all of the stones, to varying degrees, must have been contaminated with iron during the grinding process.

CONCLUSIONS

The results of this research to date demonstrate that it is technically feasible to produce high surface sorbents using a fluidized bed calcination technique at the laboratory scale. The implication is that the commercially available fluidized bed calcination units may be capable, perhaps with modification, of producing sorbents having high surface areas. Additional work will be done to determine the effect on surface area of reducing air flow to the minimum needed for fluidization, and of using a simulated combustion gas for the fluidizing medium.

Characterization of calcined reagent grade calcite by SEM and TEM suggests a fissure-like pore structure and a directional nature to the calcination controlled by crystallographic properties. If these observations are borne out on other calcined materials, they imply that the current assumption of cylindrical pores used in sulfation models and various analytical techniques is incorrect. They imply further that, with the proper combination of crystal size in the limestone and particle size in the material to be calcined, perhaps some advantage can be made of the apparent directional nature of calcination.

Particle size and elemental analyses of the raw crushed stones show an apparent significant negative correlation only between surface area and iron content. As additional data is generated, other correlations will be sought. Petrographic investigations of the raw stones will be focused on the relative amounts of sparry calcite present, as well as its crystal size and crystallographic properties such as twinning.

ACKNOWLEDGMENTS

Connie Turlington of Northrop Services, Inc., assisted by Linda Harry, was responsible for generating the laboratory data. Their efforts and technical input have proven invaluable. Thomas Nuhfer of Carnegie-Mellon University provided the SEM photos. Howard Wagenblast and Margaret Nasta of Mellon Institute directed the TEM analysis. Limestone samples were donated through the cooperation of the following companies: Commercial Minerals Company, Inc., Newark, CA; Chemical Lime, Inc., Fort Worth, TX; Round Rock Lime Co., Blum, TX; Longview Lime Co., Saginaw, AL; Dravo Lime, Maysville, KY; and Genstar Cement and Lime Co., Henderson, NV. Daniel A. Textoris, Department of Geology, University of North Carolina, Chapel Hill, NC, lent guidance in the petrographic interpretations.

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2. R. D. Harvey, R. R. Frost and J. Thomas. "Petrographic Characteristics and Physical Properties of Marls, Chalks, Shells and Their Calcines Related to Desulfurization of Flue Gases." EPA-650/2-73-044 (NTIS PB226321), September 1973.

3. S. J. Gregg and K. S. W. Sing. Adsorption, Surface Area and Porosity. New York, NY: Academic Press, 1967.

4. R. L. Folk. Petrology of Sedimentary Rocks. Austin, TX: Hemphill's, 1968.

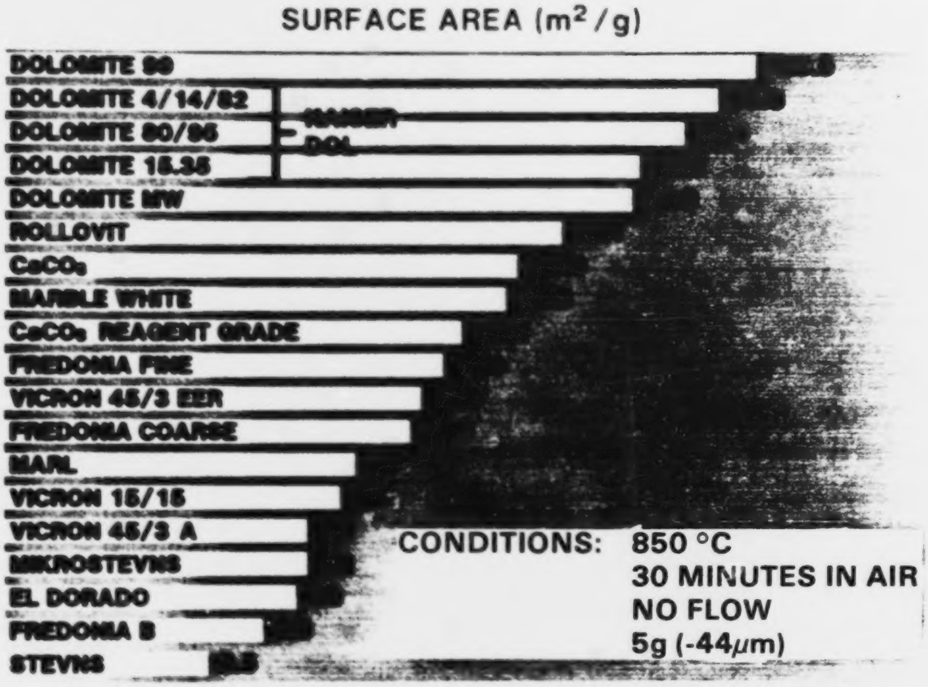

Figure 1. B.E.T. surface areas of -44 μm materials.

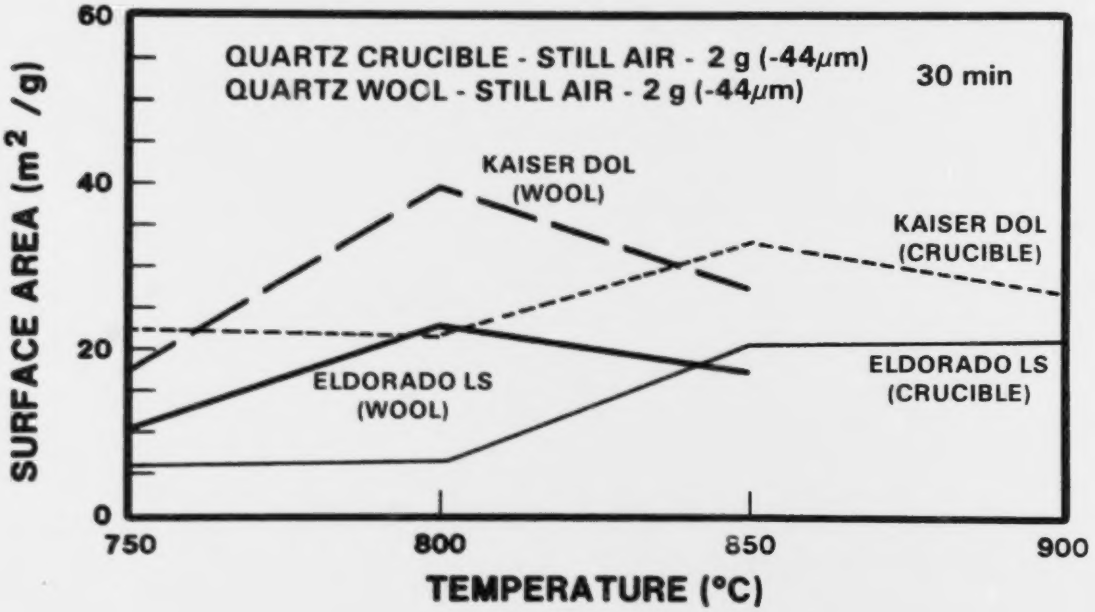

Figure 2. Results of calcination in crucibles vs. calcination on quartz wool.

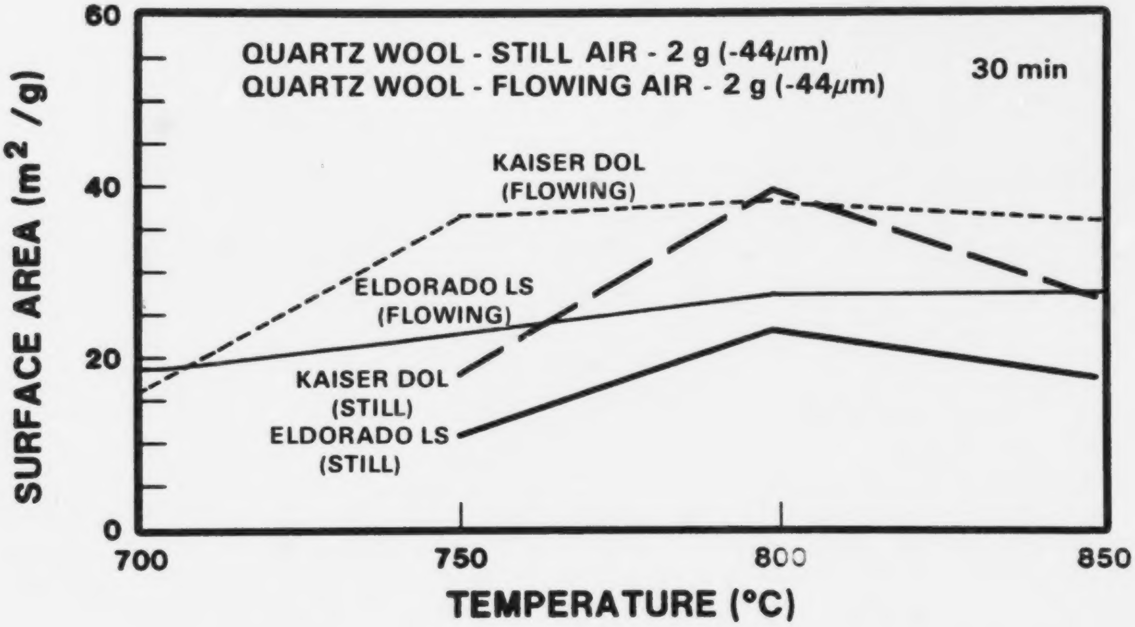

Figure 3. Results of calcination in still air vs. flowing air.

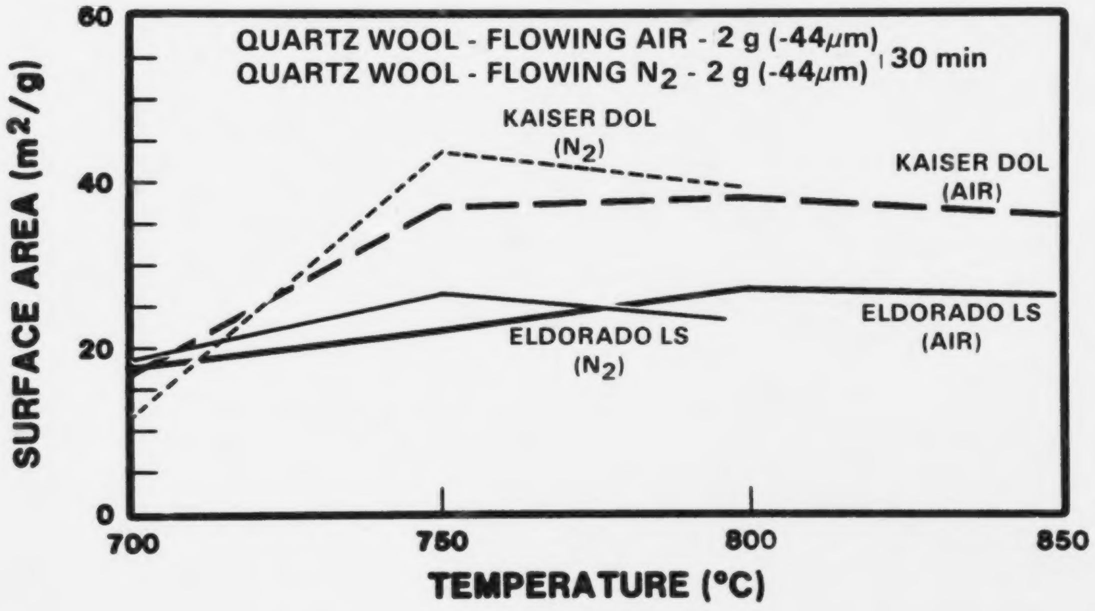

Figure 4. Results of calcination in flowing air vs. flowing nitrogen.

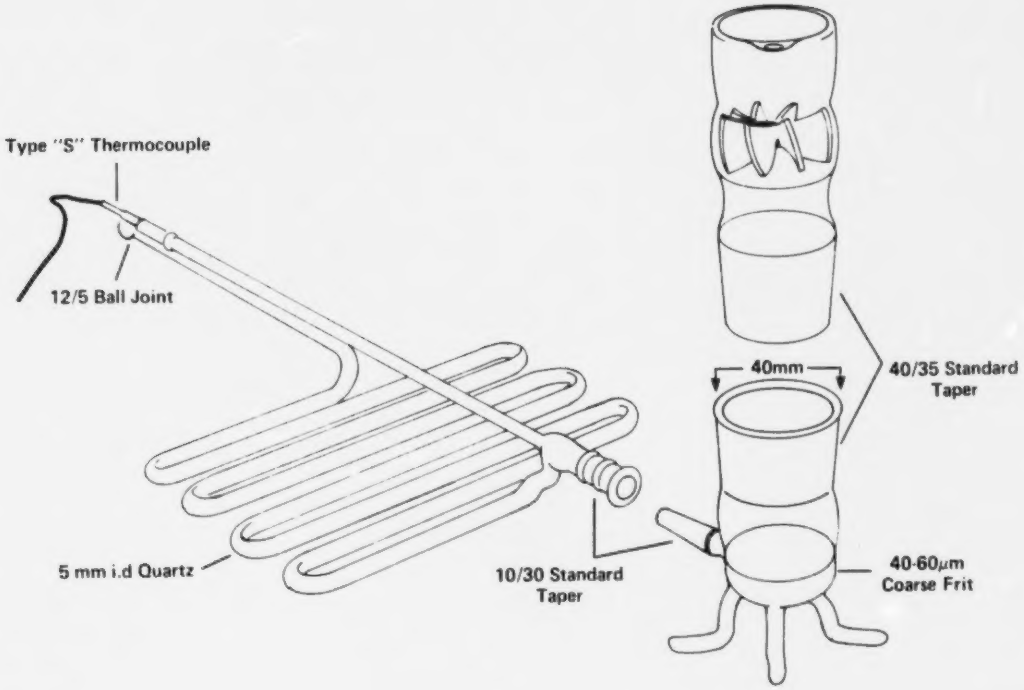
Type "S" Thermocouple
12/5 Ball Joint
5 mm i.d Quartz
10/30 Standard Taper
40mm
40/35 Standard Taper
40-60μm Coarse Frit

Figure 5. Fused quartz fluidized bed calcination unit.

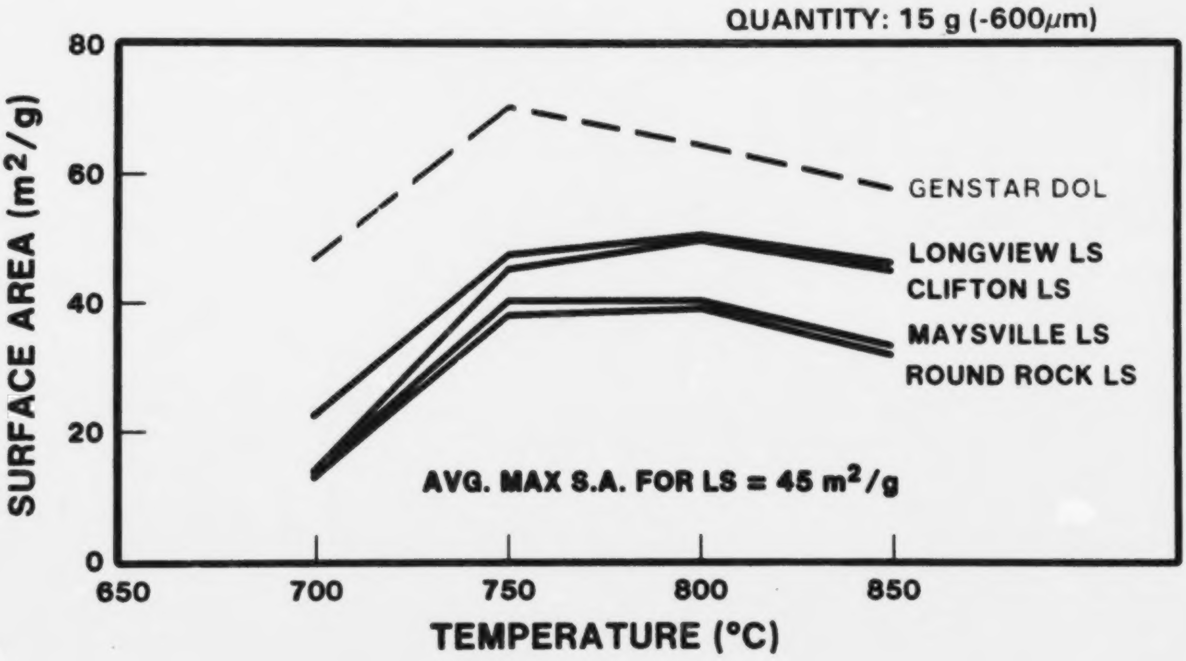

Figure 6. Results of calcination by fluidization in nitrogen for 30 minutes.

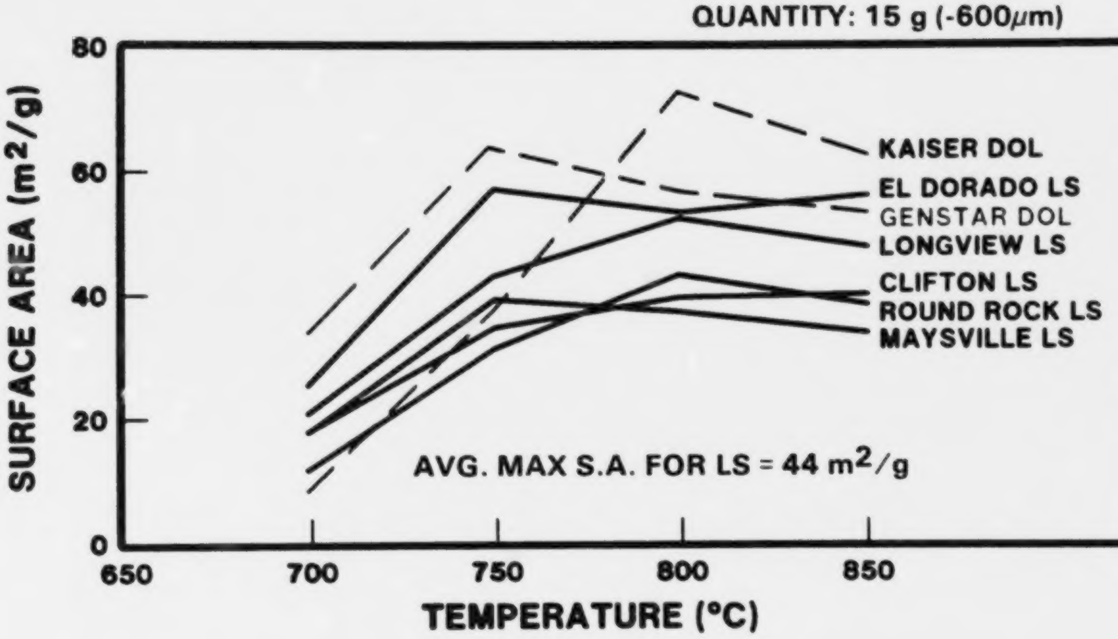

Figure 7. Results of calcination by fluidization in air for 30 minutes.

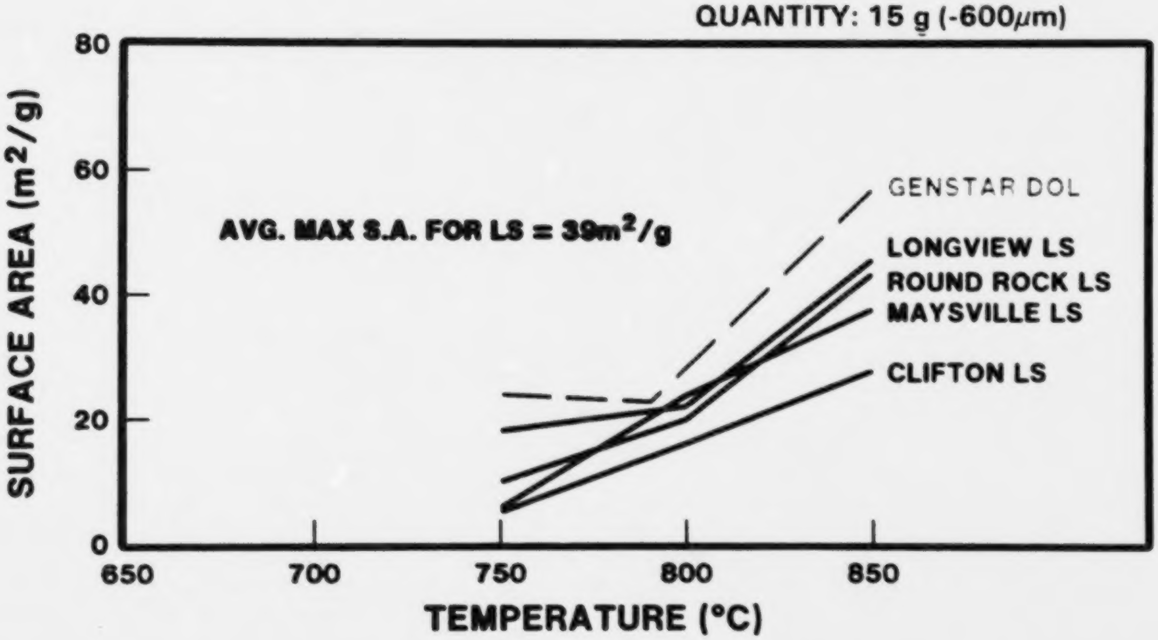

Figure 8. Results of calcination by fluidization in nitrogen for 15 minutes.

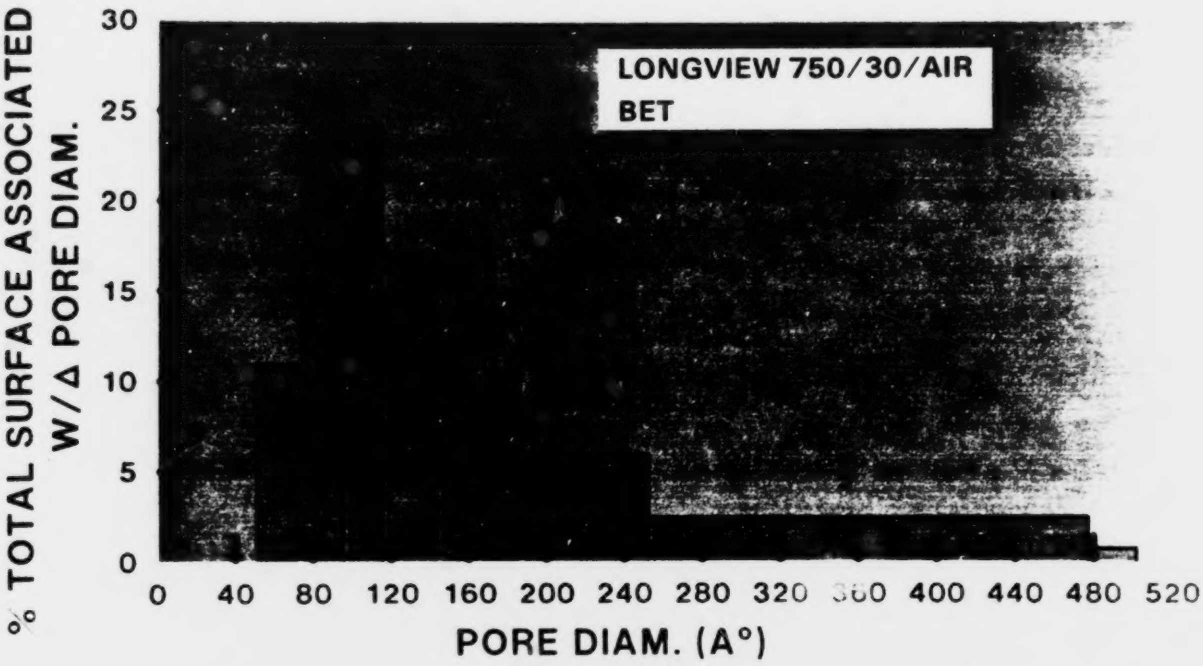

Figure 9. Percent of total surface area associated with pore size increments by B.E.T.

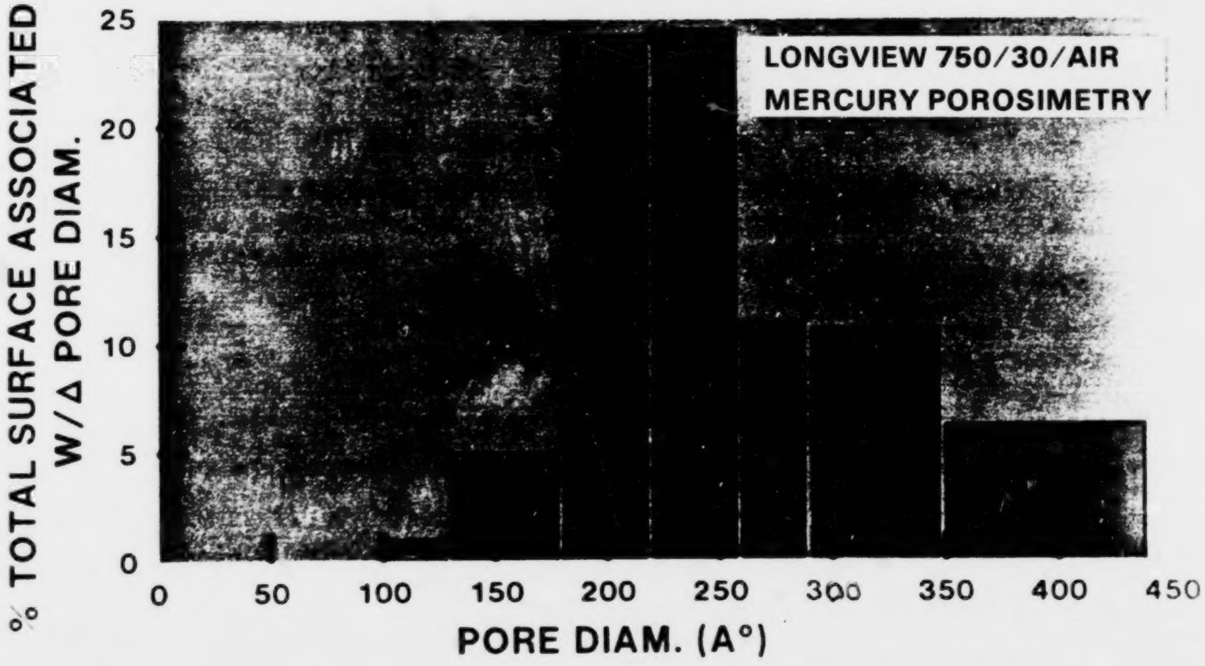

Figure 10. Percent of total surface area associated with pore size increments by porosimetry.

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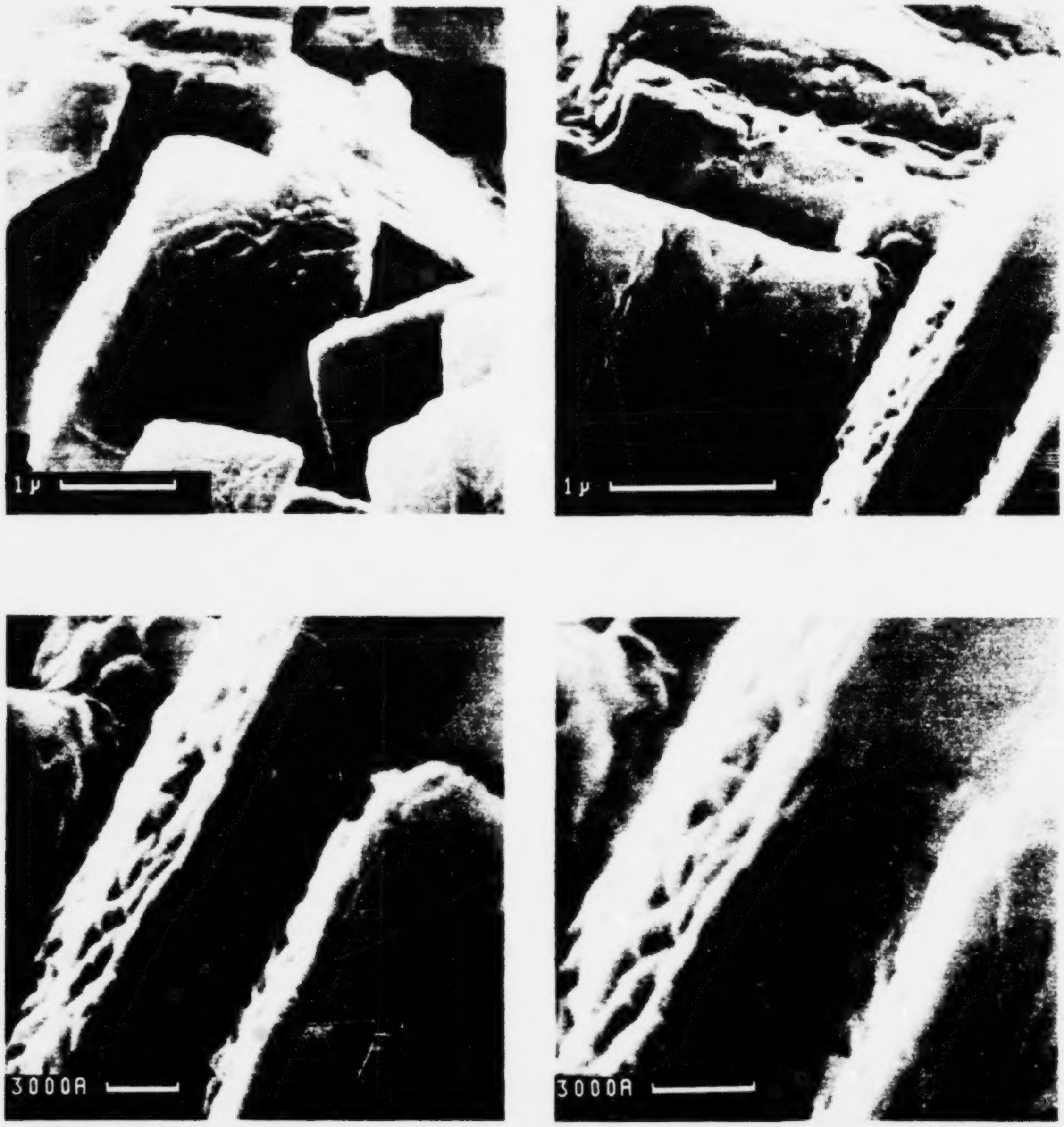
1 μ
1 μ
3000A
3000A

Figure 11. SEM photographs of calcined reagent grade calcite.

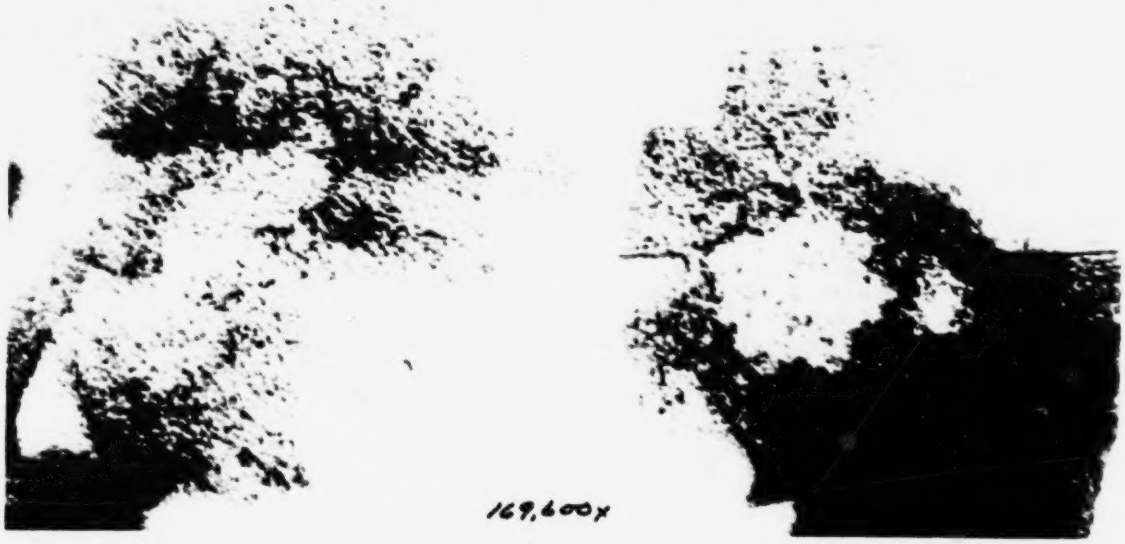

Figure 12. TEM photograph of calcined Maysville limestone.

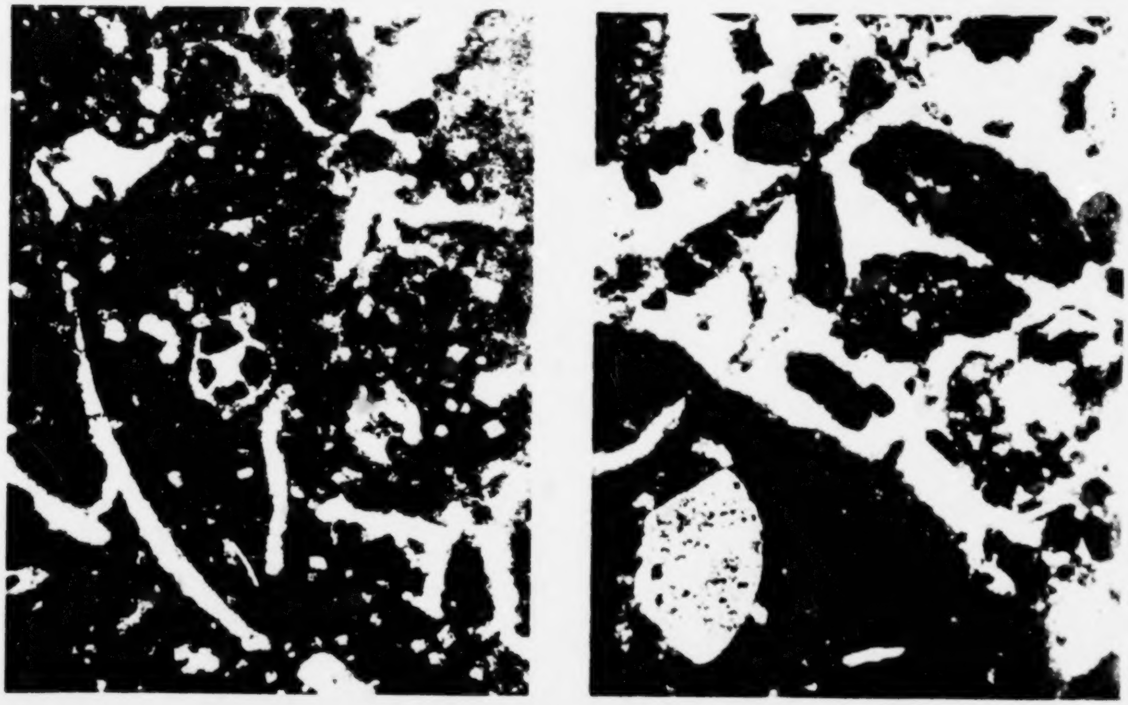

Figure 13. Photomicrographs of thin-sectioned Maysville limestone (picture width = 2 mm).

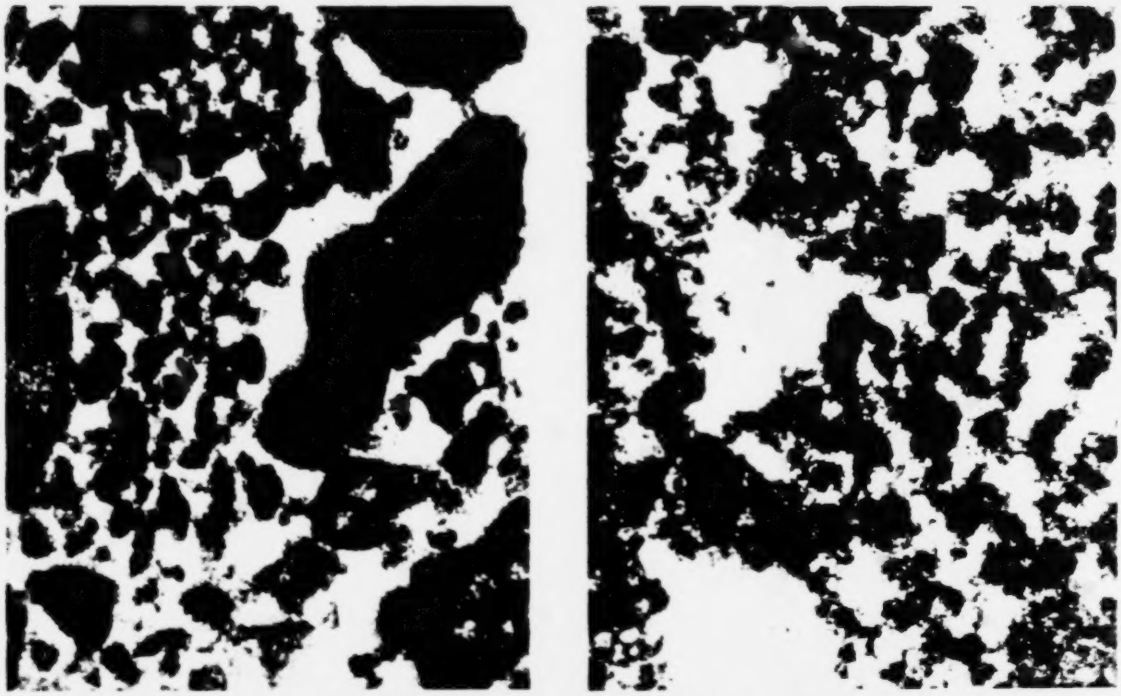

Figure 14. Photomicrographs of thin-sectioned Longview limestone (picture width = 2 mm).

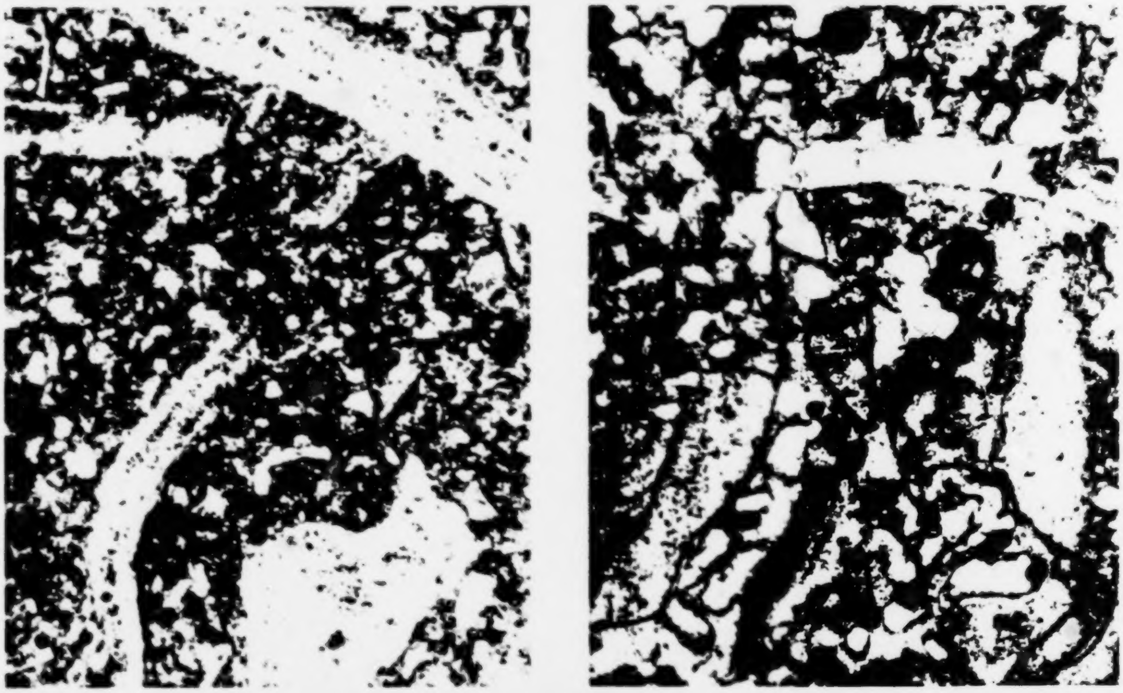

Figure 15. Photomicrographs of thin-sectioned Clifton limestone (picture width = 2 mm).

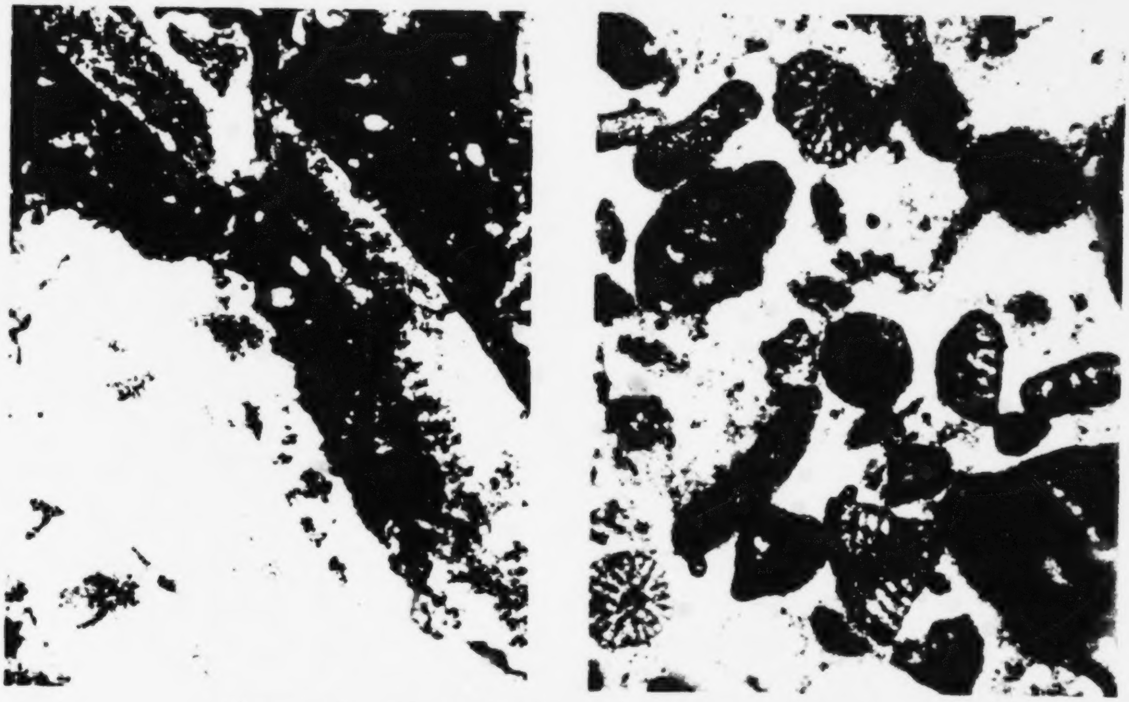

Figure 16. Photomicrographs of thin-sectioned Round Rock limestone (picture width = 2 mm).

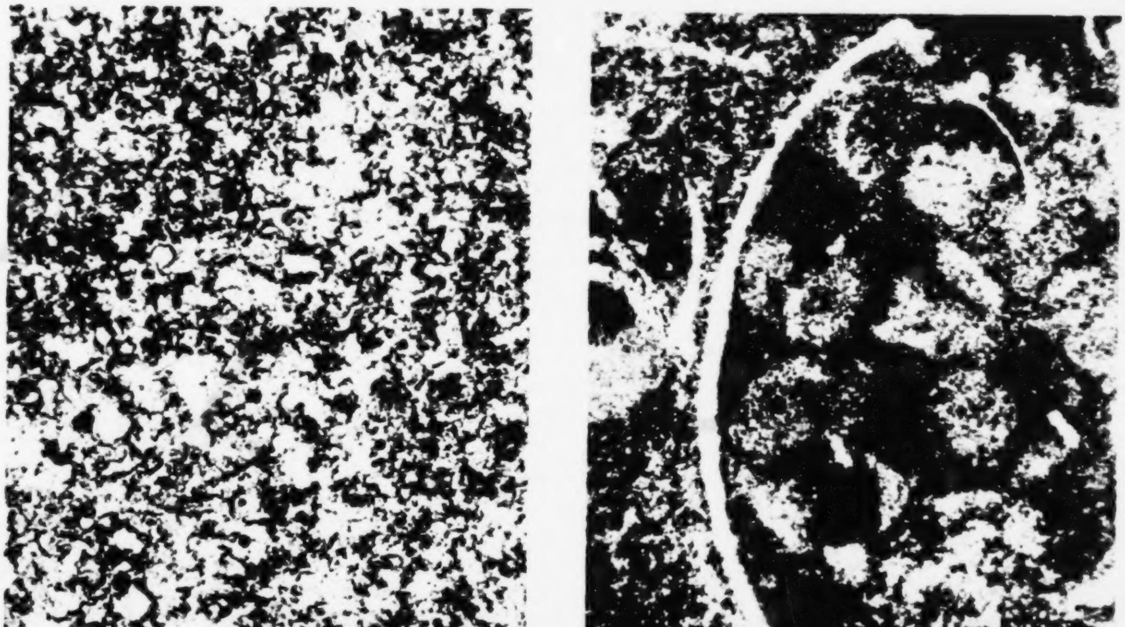

Figure 17. Photomicrographs of thin-sectioned Genstar dolomite (picture width = 2 mm).

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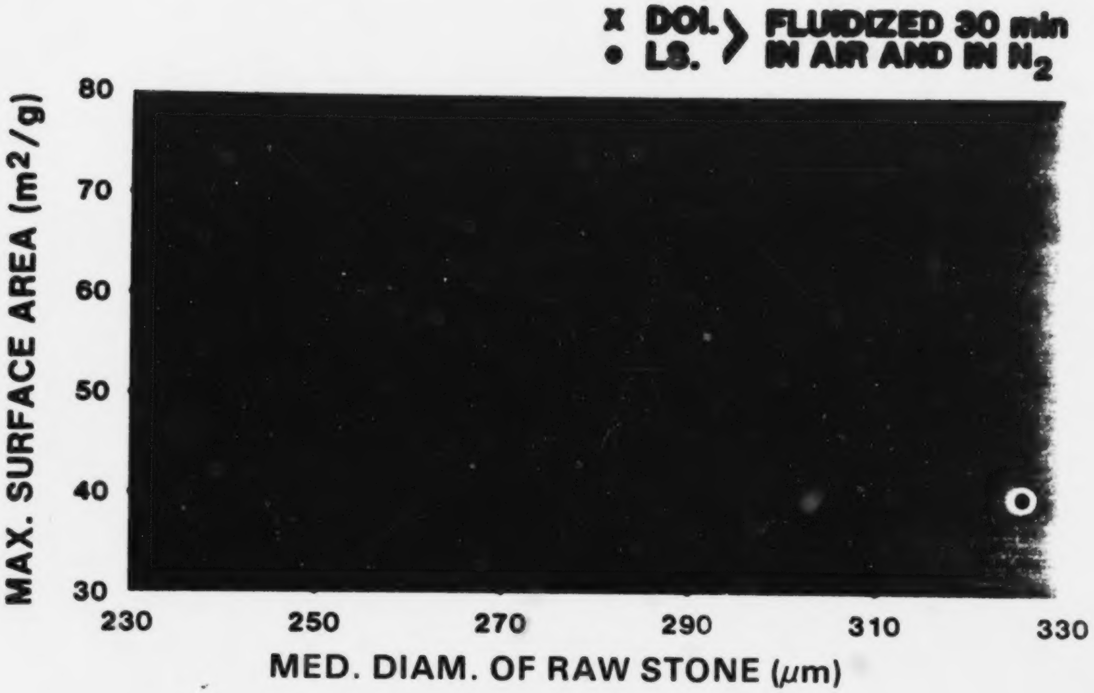

Figure 18. Scatterplot of maximum surface areas in air and in nitrogen vs. median particle diameter of raw stone.

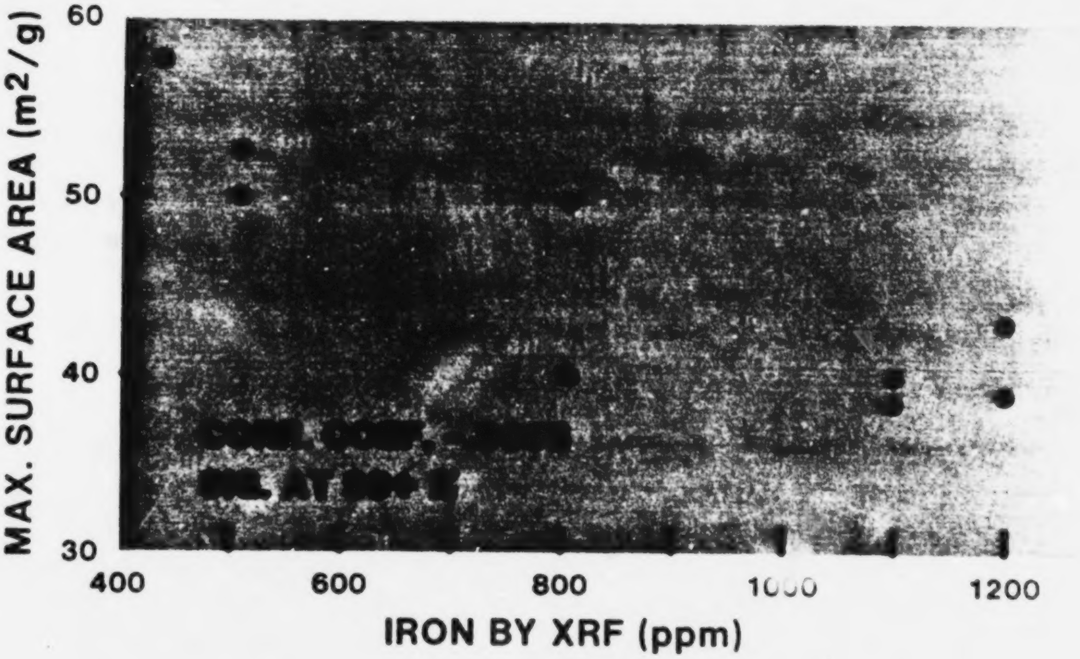

Figure 19. Scatterplot of maximum surface areas in air and in nitrogen vs. iron content of stone.

Table 1

B.E.T. AND TGA ANALYSES OF FLUIDIZED BED SAMPLES

Atm.	Time (min.)	Temp. (°C)	Maysville		Clifton		Round Rock		Longview		Genstar		El Dorado		Kaiser	
			TGA*	BET**	TGA	BET	TGA	BET	TGA	BET	TGA	BET	TGA	BET	TGA	BET
N_2	30	700	25	12.9	49	13.5	26	12.4	39	21.5	67	46.5				
		750	97	40.0	95	44.8	94	38.2	92	47.0	100	69.2				
		800	100	39.8	100	49.9	100	39.3	100	49.8	100	64.2				
		850	100	33.6	100	44.8	100	31.9	100	45.7	100	57.6				
Air	30	700	32	17.0	58	17.6	32	11.0	42	20.1	85	33.1	13	24.8	6	7.6
		750	95	39.8	67	35.1	67	31.7	94	43.1	100	64.8	100	58.1	59	37.1
		800	100	37.4	100	39.8	100	43.1	100	53.0	100	57.8	100	53.5	100	74.0
		850	100	34.3	100	40.3	100	38.6	100	48.0	100	54.2	100	56.6	100	63.6
N_2	15	700									20	27.0				
		750	15	5.4	28	4.9	28	9.7	19	18.0	31	24.0				
		800	94	24.0	58	16.0	77	20.0	94	22.0	42	23.0				
		850	100	39.0	100	28.0	95	45.0	96	47.0	98	59.0				

* Percent calcination
** m^2/g

Table 2

SIZE DISTRIBUTION OF FLUIDIZED BED SAMPLES*

Screen Size (μm)	Genstar	Maysville	Longview	Clifton	Round Rock	Kaiser	El Dorado
595	5.4	7.6	4.2	3.8	3.9	1.6	3.9
354	40.1	38.0	36.1	30.5	36.6	29.4	33.1
250	12.3	14.7	12.7	16.2	15.8	21.2	15.0
149	16.5	17.1	19.6	20.4	17.9	21.2	17.4
88	8.6	9.7	11.3	11.9	10.9	11.7	11.7
44	9.7	9.0	9.2	10.4	9.3	11.0	12.5
<44	6.7	3.9	6.0	6.6	5.2	2.8	5.2
Median Diam.	311	325	278	255	300	250	267

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* Expressed as percentage of material equal to or greater than screen size but less than next larger screen size.

Table 3

X-RAY FLUORESCENCE ANALYSES OF FLUIDIZED BED SAMPLES*

Elements	Genstar	Maysville	Longview	Clifton	Round Rock	Kaiser	El Dorado
Magnesium (%)	11.8	1.49	0.44	0.35	0.23	9.01	0.36
Aluminum	720	1800	1000	460	970	64	480
Silicon	2200	7500	2200	1400	2300	1300	1500
Phosphorous	0.0	0.0	7	0.0	0.0	140	490
Sulfur	190	510	300	280	250	130	190
Chlorine	740	280	5	4	0.0	75	0.0
Potassium	300	600	240	29	16	1	29
Calcium (%)	23.4	39.8	39.0	41.1	40.7	20.6	37.0
Titanium	110	9400	57	19	31	28	55
Iron	2500	1100	510	810	1200	1600	450
Nickel	21	11	8	13	74	12	17
Copper	46	38	35	39	52	21	42
Zinc	14	0.0	0.0	0.0	0.0	2	4
Rubidium	54	73	72	79	75	5	70
Strontium	82	31	180	160	370	93	230
Barium	70	120	0.0	18	0.0	0.0	0.0

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* ppm except when noted otherwise.

REACTIVITY OF CALCIUM-BASED SORBENTS FOR SO_2 CONTROL

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ABSTRACT

Laboratory-scale controlled-temperature experiments were used to study aspects of SO_2 capture by limestone sorbents in a flame-gas environment. Experimental parameters were sorbent type, temperature, residence time, and the effects of mineral additives, or promoters, on sorbent reactivity. The data revealed that isothermal capture is greatest at 1000°C, and that above 1000°C sintering of the limestone can occur which reduces the sorbent utilization. High surface area precalcined sorbents achieved moderately higher ultimate utilizations than their parent carbonates, but their real advantage was more rapid sulfation at lower temperatures where raw stones were limited by calcination. At 900 and 1000°C the time for calcination of carbonate sorbents was significant. Pressure hydrated (type S) dolomite limes consistently achieved the highest utilizations. The results suggest that--at ideal sulfation conditions (1000°C, isothermal residence times greater than 1 second, no deactivation of the sorbent by coal ash minerals)--the best calcium utilizations achievable would be about 25-30% with the raw limestone tested (Vicron 45-3), about 30-35% with the raw dolomite tested, and about 40% with precalcined dolomite (precalcined to a surface area of 60 m^2/g) and with pressure-slaked dolomitic lime. The addition of Cr_2O_3, alkali metal salts, and certain other promoters increased the utilization of limestone. Cr_2O_3 effected a factor of 3.5 increase in utilization after calcination at 1600-1700°C.

INTRODUCTION

Dry-limestone injection provides an economically attractive means for controlling SO_2 emissions in pulverized-coal-fired (p.c.) utility boilers. The process is especially attractive as a retrofit for older boilers because of the potentially low capital costs relative to other SO_2 control technologies (1). In addition, the raw material is readily available and relatively inexpensive (2). Early demonstration tests in the late 1960's and early 1970's, however, met with little success (3) in that acceptable levels of SO_2 removal could not be achieved, even with a large stoichiometric excess of limestone. The present effort was undertaken in order to investigate the conditions which will optimize

SO_2 removal from flue gases by calcium-based dry sorbent injection. The conditions which were explored included time, temperature, sorbent type and preparation, and the effects of mineral additives on sorbent performance.

Previous efforts have examined the overall process of SO_2 capture within the confines of the conditions present in full-scale systems (4,5). Both calcination (6) and sulfation kinetics (7,8) have also been studied in fundamental experiments and have been addressed theoretically (9-11). The calcination of various limestones has been examined with regard to the properties -- surface area, porosity, pore size, etc. -- which are most likely to affect the reaction with SO_2 (12-16). Lastly, the interactions of limestones with other minerals (17, 18) which are found in coals and their effects on SO_2 capture, both positive (19, 20) and adverse (14, 21), have been investigated in recent years.

The present paper examines the SO_2 capture process in light of past efforts. It does so under experimental conditions which simulated the thermal and chemical environment of a p.c. utility boiler. The experimental objectives were to provide conditions for sorbent injection which were representative of those in large-scale systems, but which were well characterized, uniform, and reproducible. The needs addressed by this work were:

- To determine the so-called "reactivity" of a wide variety of sorbents. Reactivity refers to the ability of a sorbent to uptake sulfur under dispersed-phase high-temperature conditions which would exist in utility furnaces. The reactivities of a number of sorbents including high surface area precalcines were determined in a single experimental system.

- To examine the reactions of calcination and sulfation in the dispersed phase at the high temperatures and short residence times which are representative of those encountered in p.c. utility boilers.

- To study the effects of mineral matter interactions on the ability of limestone to remove SO_2.

- To observe physical changes which could be linked to either reactivity or the ability of the sorbent to uptake sulfur.

The approach applied to these needs was to inject sorbents into the high temperature environment of a laboratory gas flame. Both isothermal and non-isothermal environments were provided from which the sorbents were sampled and analysed to determine their physical and chemical properties. The sorbents were sulfated both in-situ during calcination and external to the reactor. In the external sulfation experiment, sulfation occurred in the dispersed phase, in an environment which was independent of the reactor conditions, thereby decoupling sulfation from heatup and calcination. An attempt was then made to link the physical properties of the sorbents to their abilities to absorb sulfur under a variety of conditions.

EXPERIMENTAL

Apparatus and Conditions

Flame Thermal Decomposition. Two experimental reactors were employed in this program. The first is a flame reactor which was used to examine flame processing of sorbents at high temperatures (>1200°C) and short times (<250 ms). This reactor (Figure 1) consists of a porous-bronze-plug flat-flame burner downfired into a 10 cm x 10 cm stainless steel chimney with optical, thermocouple, and solids-sampling access. Limestones were injected into the reactor through a 0.64 cm i.d. copper tube mounted axially through the burner. Solids were entrained in a fuel/air premixture prior to injection in order to ensure rapid heating to peak reactor temperature. Heat loss through the reactor walls then resulted in a steep temperature dropoff. Injection of the solids was accomplished with a Smith-type fluidized bed feeder and off-take tube assembly (22, 23).

Reactivity toward SO_2 was determined using a dispersed-phase quartz SO_2 reactivity probe. Samples of dispersed sorbent--now calcined in the flame reactor, but not yet sulfated--were collected at the top of the probe and quenched slowly (10^4 K/s) to 650°C. At this point, the calcined sorbent sample stream entered a reaction zone which was heated to 1100°C. In the reaction zone, 6 percent SO_2 was added and the sample stream allowed to react for 0.6 s. The sample then was quenched and collected on a glass fiber filter at 130°C.

Isothermal Reactor. The second reactor is a dispersed-phase isothermal reactor (ITR). The ITR provides a relatively long (up to 3.0 s) isothermal zone in which sorbent chemistry can be studied as a function of time, temperature, and environment. This reactor is unique because it provides a large volume for dispersal of sorbents at reasonable feed rates. This is necessary to permit solids sampling for chemical analysis within practical time frames. The ITR (Figure 2) is an electrically heated, drop-tube furnace into which flame gases are downfired. It has a heated length of 90 cm and accommodates a 10 cm diameter alumina reaction tube. The ITR has a maximum wall temperature of 1500°C.

The test gas for the ITR is produced by a burner identical to the one used with the flame thermal decomposition reactor. Limestone was injected into the ITR along the axis of the reactor through the burner. The limestones were injected from a 1.1 mm i.d. tube, which produced a turbulent jet, effectively and rapidly dispersing the materials over a wide cross-section of the reactor. Residence times and heating rates of the particle streams were calculated based on confined jet mixing theory (24) and convective and radiative heat transfer calculations. Heating rates were on the order of 10^4 K/s and total (end of reactor) residence times of 1.2 - 1.6 s were available for the experiments described here. Solids sampling from the ITR was accomplished with an isokinetic water-cooled stainless steel probe. Sorbents were quenched rapidly in the probe and collected on a glass fiber filter located at the base of the probe. Sampling times and temperatures were selected so that sulfur uptake by the sorbent on the filter holder was insignificant. The probe is 1.2 m long and enables sample collection within 40 cm of the sorbent injection location, thus permitting sampling of the dispersed sorbent after short (~ 250 ms) residence times.

Temperature profiles in the ITR are shown in Figure 3. Temperatures were measured using a 0.025 mm diameter type S thermocouple. Radiation corrections to the thermocouple readings were applied only for the flame thermal decomposition reactor and for non-isothermal conditions in the ITR. Otherwise the corrections were smaller than ±5 K. The profiles in Figure 3 are all for hydrogen/air flames. Methane was used for flame temperatures above 1350°C.

Sorbent Precalcination Apparatus. In order to generate high-surface-area precalcined materials for testing in both the TDR and ITR, the transpirated bed calciner shown in Figure 4 was developed. The apparatus in Figure 4 is a 20-cm diameter stainless-steel can placed inside a large box furnace. The can is fitted with a heavy lid which has a single hole for thermocouple access and to allow sweep gas and CO_2 to escape. Limestone is spread in a thin bed on a 400 mesh stainless steel screen. Beneath the screen is a spiral made from 6.4 mm stainless steel tubing. The spiral has small holes drilled on the underside and acts as a flow distributor for the transpiration gas. The transpiration gas, N_2, is preheated by passing it through a long coil of stainless steel tubing located inside the box furnace.

Operation of the transpirated bed calciner consists of passing nitrogen through the bed of powdered limestone at high temperature. The mass of limestone and flow of nitrogen are balanced to provide the shortest practical calcination time at the lowest possible temperature. Typical operating conditions are 700°C, 60 g limestone, 0.55 l/s N_2. Carbon dioxide evolved resulting from calcination is swept away from the limestone by the nitrogen, thereby lowering the local CO_2 concentration and accelerating the calcination rate. For both Vicron 45-3 and D3002 dolomite, the optimal calcination time was near 75 min.

Sorbents

Limestone samples were characterized both before and after injection using several analytical techniques which are listed in Table 1. Most of the raw materials were analysed for chemical composition, particle size distribution, and specific surface area. Samples collected from the reactors were analysed for carbon (carbonate), hydrogen (hydroxide), total sulfur (sulfate), and total calcium. From these measurements the extent of calcination and calcium utilization (percent calcium as sulfate) were determined for most samples.

The sorbents which are discussed here are listed in Table 2 along with some physical and chemical properties. Vicron 45-3 and D3002 are, respectively, the baseline calcite and dolomite in this study. They are comparable in mean size (see Table 3 for size data) and specific surface area and both are high-purity minerals. It was from these limestones that the V40 and D60 precalcines were produced. Surface areas indicated for the precalcines are typical. However, the materials were produced in small batches, and surface areas varied between batches. The Type S material is a pressure-slaked dolomitic lime manufactured by Warner.

RESULTS AND DISCUSSION

Reactivity of Flame Treated Sorbents

Figure 5 displays histograms of the reactivity for eight sorbents flame-treated in the thermal decomposition reactor at peak temperatures of a) 1200°C and b) 1500°C and then sulfated in the dispersed-phase reactivity probe at the standard 0.6 s/6% SO_2 condition. For all sorbents tested, the reactivity decreased precipitously when the flame temperature was increased. Previous measurements have indicated that this can be attributed to decreased specific surface area due to more rapid sintering at increased temperature. However, the relative reactivity of the flame-treated sorbents is insensitive to flame temperature; only the D3002 dolomite and the precalcine changed positions at the higher temperature. The limestones were generally the less reactive after flame treatment, followed by hydroxides; and the dolomites were the most reactive. A single precalcine (produced from Vicron limestone with a specific surface area of 34 m^2/gm) was tested for reactivity after flame treatment. This precalcine was found to be more reactive than the raw stone from which it was produced. Thus precalcining does have the potential for providing an increased reactivity that will not be completely lost when flame-treated for short times (<200 ms).

Isothermal Reactor

In order to investigate simultaneous calcination and sulfation of sorbents for longer times, as might occur for sorbents injected in the upper furnace, the isothermal reactor (ITR) was employed. Calcium utilization was measured as a function of residence time in the ITR for five sorbents at temperatures of 900, 1000, 1100, and 1200°C. In each case the initial SO_2 concentration in the burned gases was 3600 ppm, and the sorbent feed rate was adjusted to ensure a calcium-to-sulfur ratio (Ca/S) less than 1.0 so that the measured calcium utilization would not be affected by SO_2 depletion in the reactor.

Effects of Residence Time and Sorbent Types. At 900°C (Figure 6) the capture levels of the precalcines and Type S are all greater than those of the raw sorbents, D3002 and Vicron 45-3. In part, this is because the raw sorbents calcined slowly at this relatively low temperature, which reduced the available calcium. The Type S sorbent is suspected as having a lower calcination temperature as well as a less endothermic calcination reaction than the raw sorbents since it is a hydroxide. It may in fact calcine so quickly at 900°C that the calcination reaction presents no impediment to sulfation. The precalines (D60 and V40) are not expected to sinter (lose surface area) rapidly at this temperature. In summary, the precalcines begin to sulfate more rapidly than the raw sorbents (within 0.5 s) because they do not experience a lag time for the calcination reaction; they reach a higher ultimate utilization (at 1.0-1.5 s) because their initial high surface areas do not sinter so rapidly at this temperature, thus remaining available for sulfation.

At 1000°C (Figure 7) the relative order of reactivity has changed to: Vicron 45-3 < V40 < D3002 < D60 < Type S. This reflects a large increase in the relative reactivity of D3002. At 1.5 s the calcium utilization of D3002 is approaching that of the D60 precalcine; and, from 0.75 s on, the V40 maintains about 10 percent greater utilization than Vicron 45-3. Both of the raw sorbents exhibit some delay in SO_2 uptake, again due to calcination, but it is not as severe as that experienced at 900°C. In summary, the precalcines reach somewhat higher ultimate utilization levels than the raw sorbents but the precalcines achieve those levels in a substantially shorter time. All five sorbents display a dramatic increase in reactivity between 900 and 1000°C; evidently, the improvement in sulfation kinetics with this increase in temperature more than compensates for any increase in the rate of sintering (deactivation).

Temperature Effects. Figure 8 summarizes the sulfur capture of the five sorbents as a function of temperature. The data shown in Figure 8 were taken from utilization profiles (analogous to Figures 6 and 7) at the residence time of 1.0 s. There is very little uncertainty associated with the ranking in Figure 8 because the slopes of the calcium utilization profiles all were shallow at 1.0 s. What has not been taken into account is the delay of the onset of sulfation for Vicron 45-3 and D3002 due to slow calcination at 900 and 1000°C. Accounting for the delay would alter the shapes of the temperature/utilization curves in Figure 8 somewhat; however, it would not be reflective of the ultimate result of low-temperature injection into a p.c. utility boiler where calcination times may be a factor.

The most significant aspect of Figure 8 is the appearance of a maximum in the utilization achieved as a function of temperature. The location of the true maximum appears to be very near 1000°C but may be different for each sorbent. The maximum is thought to be a result of the tradeoff between sintering and reaction kinetics. It is interesting that the optimum temperature is the same for five different sorbents.

Sintering Rates. A grain model was used to estimate sintering rates for D60 and V40 based on the ITR sulfation data. The grain model is a mathematical model describing the sulfation of sorbent particles, assuming that the individual CaO grains within the particle are reacting according to shrinking core theory (25,26). According to the model, the rate of sulfation at any selected level of sorbent utilization is dependent upon the initial surface area (at zero utilization). By using the model to calculate the effective initial area for V40 and D60 at the various utilizations (at the various residence times) shown in Figure 7 for 1000°C (and in the analogous curves for 1100°C), it was possible to estimate how the initial surface areas of these precalcines were disappearing due to sintering as a function of residence time in the ITR. The open symbols in Figure 9 show the results of these sintering rate calculations. As shown in the figure, the effective initial surface area decreases rapidly due to sintering for both precalcines, especially at the higher temperature. For example, at 1100°C, the precalcines have lost half their effective initial surface area in less than 0.25 s. The apparent sintering at 1000°C is not as severe. For example, almost 1.0 s is required at the lower temperature in order to lose half of the initial precalcine surface area; significant sulfation could occur within that time before the area is lost.

In addition to the physical loss of BET surface area due to thermal sintering, there would be a loss of reactive surface area due to sulfation (as reactive CaO sites were converted to $CaSO_4$). The closed symbols in Figure 9 show the calculated loss of "reactive surface area" due to sulfation as a function of residence time, based upon the sulfation levels measured in the ITR experiments (e.g., Figure 7). As indicated by the comparison of the closed and open symbols in Figure 9, the loss of area due to thermal sintering is much more severe than the loss of reactive area due to sulfation of CaO sites. (The sulfation reaction might also reduce the BET surface area by plugging the interstices between grains, as the CaO structure expands to become $CaSO_4$. The grain model does not account for such sulfate plugging. In fact, the BET area loss indicated by the open symbols in Figure 9 is due not only to thermal sintering, but also to sulfate plugging of the interstices or pores.

Sorbent Reactivity Promoters

Figure 10 shows calcium utilization for Vicron 45-3 injected alone, and mixed with 6 percent-by-weight Cr_2O_3, into the ITR. For these tests, the ITR was operated at a constant furnace temperature of 1100°C, but the flame temperatures were varied as shown, resulting in a ramped temperature profile from flame temperature to 1100°C. All tests employed 3600 ppm SO_2. As expected, the utilization of Vicron 45-3 decreased with increasing flame temperature. This reflects both a decrease in surface area upon calcination, and in some cases, a shorter residence time in the sulfation window where sulfation will occur with reasonable kinetics (approximately 1250 to 1000°C). With the Vicron/Cr_2O_3 mixture, however, the utilization initially increased as the flame temperature was increased. Subsequently, the utilization decreased until, at a 1950°C flame temperature, the utilization was nearly equal to that of Vicron 45-3 alone. By comparing the utilization of Vicron 45-3 with that of the Vicron/Cr_2O_3 mixture, enhancement factors were obtained as shown in Figure 11. The enhancement factor is a relative increase in utilization due to the addition of Cr_2O_3. The enhancement is greatest, a factor of 3.5, at 1600-1700°C flame temperature. Both the temperature and the magnitude agree with data obtained in a bench-scale boiler simulator furnace (27).

Additional Minerals. Fourteen additional minerals were examined in a series of screening tests in order to determine their potentials as sorbent reactivity promoters. The materials, in 5 percent-by-weight mixtures with Vicron 45-3, were exposed to 3600 ppm SO_2 under the 1100°C isothermal condition as well as with a 1360°C flame fired into the ITR at a furnace temperature of 1100°C.

Figure 12 shows the results of isothermal tests at 1100°C in bar-graph form. The open section of each bar is the utilization achieved in 0.92 s; the shaded portion represents the additional utilization up to 1.4 s. The horizontal lines are the averages of four replicates of the utilizations measured for unpromoted Vicron 45-3 at the two residence times. Down-pointing vertical arrows adjacent to the data for Na_2SO_4, K_2SO_4, and MoS_2 show what their calcium utilizations would be if the sulfur initially present in the additives remained with the additive, and was not released by the additive and captured by the calcium. For the Li_2CO_3 mixture, the utilization measured at 1.4 s was lower than that at 0.92 s.

Every additive tested, except MoS_2, caused a net increase in utilization (compared with unpromoted Vicron) after 1.4 s. The magnitudes of the increases are not as great as were observed with Cr_2O_3; however, all of the results are above the 95 percent confidence limit based on the four replicate samples of Vicron 45-3 collected at 1.4 s.

The same promoters were tested under nonisothermal conditions using a 1360°C flame with the ITR still at 1100°C. Results of these tests are shown in Figure

13. The calcium utilization by Vicron 45-3 was considerably lower at this condition than at 1100°C. This was due in part to thermal deactivation but also stems from the substantially shorter time that the sorbent had in the sulfation window. The total residence time of the sorbent in the flame was 0.6 s; however, much of this time the temperature was above 1250°C. Calcium utilization by many of the mixtures was quite high compared with Vicron 45-3. Only three additives, TiO_2, MoS_2, and V_2O_5, had no beneficial effect on calcium utilization within 95 percent confidence. After correction for its initial sulfur content, utilization by the MoS_2 sample actually lay below the 95 percent confidence interval for the five Vicron 45-3 samples collected. Platinum and V_2O_5, both oxidation catalysts, had little effect. The alkali metal salts as a group showed the most promise as promoters; and lithium, the lightest alkali, produced the greatest enhancement.

CONCLUSIONS

The reactivity of flame-treated sorbents was found to be strongly affected by both temperature and sorbent type. The results of this work, showing a loss of reactivity with increasing calcination temperature, were consistent with results seen in a prior study (28). The general order of sorbent reactivity, in terms of calcium utilization, was: dolomites > hydroxides > calcites.

For simultaneous calcination and sulfation under lower temperature isothermal conditions, precalcines and a pressure-hydrated dolomite had the greatest initial reactivity. At longer times and higher temperatures, however, the advantages of precalcines diminished. In general, dolomitic materials were more reactive than calcitic stones; and the most reactive material tested was a pressure-slaked dolomitic lime. The advantage of the dolomitic lime may have been due, in part, to a small mean particle size (about 1 m mass mean, compared to about 10 m for the calcite and dolomite) suggesting a need for better characterization of sorbent size and size distribution. For all of the sorbents tested, the optimum temperature for isothermal SO_2 capture was 1000°C. The precalcines sintered rapidly at higher temperature, offsetting any increased reaction rate and diminishing their reactivity.

Sorbent reactivity was enhanced by the addition of several mineral additives. The greatest improvement was seen with Cr_2O_3. An injection temperature of 1600-1700°C induced the maximum increase in capture with Cr_2O_3, relative to unpromoted limestone at that temperature. Alkali metal salts also promoted SO_2 sorption by lime. With the alkalis, however, a substantial improvement in utilization was observed only by using an injection temperature of 1360°C. However, the promoted utilizations at 1360°C were still generally less than unpromoted utilization at 1100°C. Enhancement of SO_2 sorption by alkalis increased with decreasing formula weight of the additive.

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Table 1

ANALYTICAL PROCEDURES

PROCEDURES	DETERMINATION
Brunauer, Emmett, Teller N_2 absorption isotherm	Specific Surface Area
Perkin-Elmer 240B Extent of calcination, hydration	Carbon, hydrogen determination
Leco SC32 Instrumental Sulfur Analyser	Total Sulfur (S^{--}, SO_3^{--}, SO_4^{--}, S)
ASTM D2795 Chelometric titration	Total Calcium
Sedigraph (X-ray sedimentation)	Particle size distribution, mean size
Mercury instrusion porisimetry distribution	Pore size distribution, true porosity, porosity

Table 2

PHYSICAL AND CHEMICAL PROPERTIES OF LIMESTONE SORBENTS

Material	Composition	Mean Size μm	Surface Area m^2/g	Chemical Analysis, wt%	
				Ca	Mg
Vicron 45-3	$CaCO_3$	11	0.6	39.0	0.49
Dolomite (Pfizer)	$CaCO_3 \bullet MgCO_3$	34	0.9	21.0	12.1
D3002 Dolomite	$CaCO_3 \bullet MgCO_3$	12	0.54	24.8	11.3
D60 Precalcine	$CaO \bullet MgO$	--	60.67	---	---
V40 Precalcine	CaO	--	41.45	---	---
Type S (Warner)	$Ca(OH)_2 \bullet Mg(OH)_2$	1.0	18.20	28.0	15.9
M and M Limestone	$CaCO_3$	6	1.1	---	---
German Hydroxide	$Ca(OH)_2$	--	14	---	---
RWE Hydroxide	$Ca(OH)_2$	--	26	---	---
Fisher Hydroxide	$Ca(OH)_2$	12.5	13	54.0	0.3

Table 3

PARTICLE SIZE DISTRIBUTIONS OF RAW SORBENTS

Equivalent Spherical Diameter, μm	Mass Percent Finer	
	Vicron 45-3	D3002 Dolomite
80	100	100
50	100	99
30	95	97
20	80	80
10	46	42.5
8	37	35
5	24	21
3	14.0	13.5
2	8.5	10
1	3.0	5.5
0.8	2.5	4.5
0.5	1.0	3.0
0.3	---	1.0

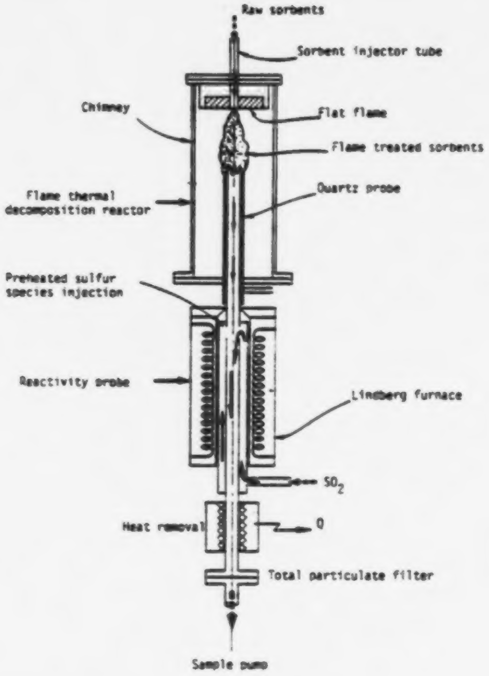
Raw sorbents
Sorbent injector tube
Chimney
Flat flame
Flame treated sorbents
Quartz probe
Flame thermal decomposition reactor
Preheated sulfur species injection
Reactivity probe
Lindberg furnace
SO_2
Heat removal
Q
Total particulate filter
Sample pump

Figure 1. Schematic of the dispersed-phase SO_2 reactivity probe as installed in the flame reactor.

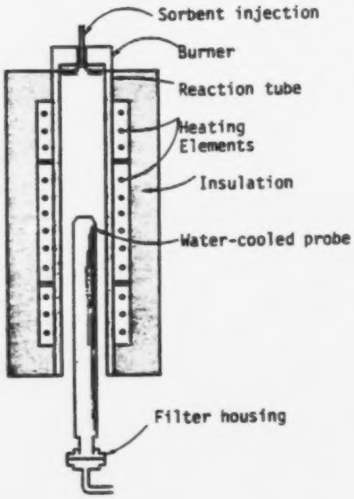
Sorbent injection
Burner
Reaction tube
Heating Elements
Insulation
Water-cooled probe
Filter housing

Figure 2. Schematic of the isothermal reactor with the burner and water-cooled probe installed.

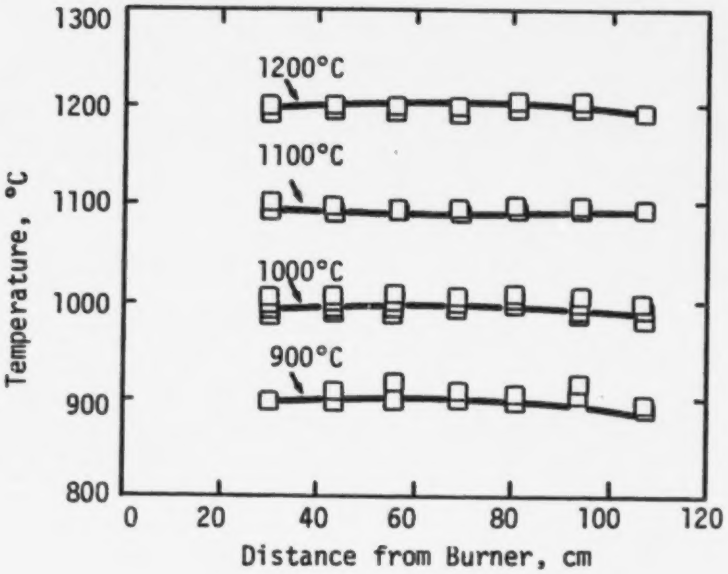

Figure 3. Temperature profiles in the isothermal reactor.

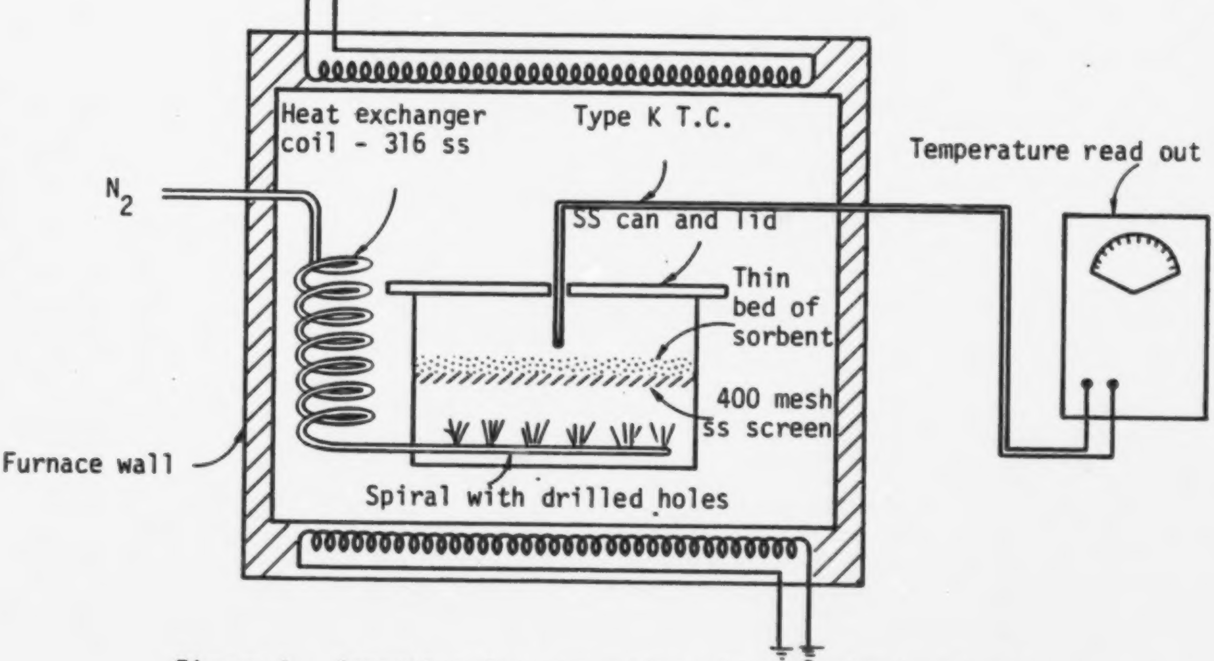
Heat exchanger coil - 316 ss
Type K T.C.
Temperature read out
N$_2$
SS can and lid
Thin bed of sorbent
400 mesh ss screen
Furnace wall
Spiral with drilled holes

Figure 4. Apparatus for generation of precalcined sorbents.

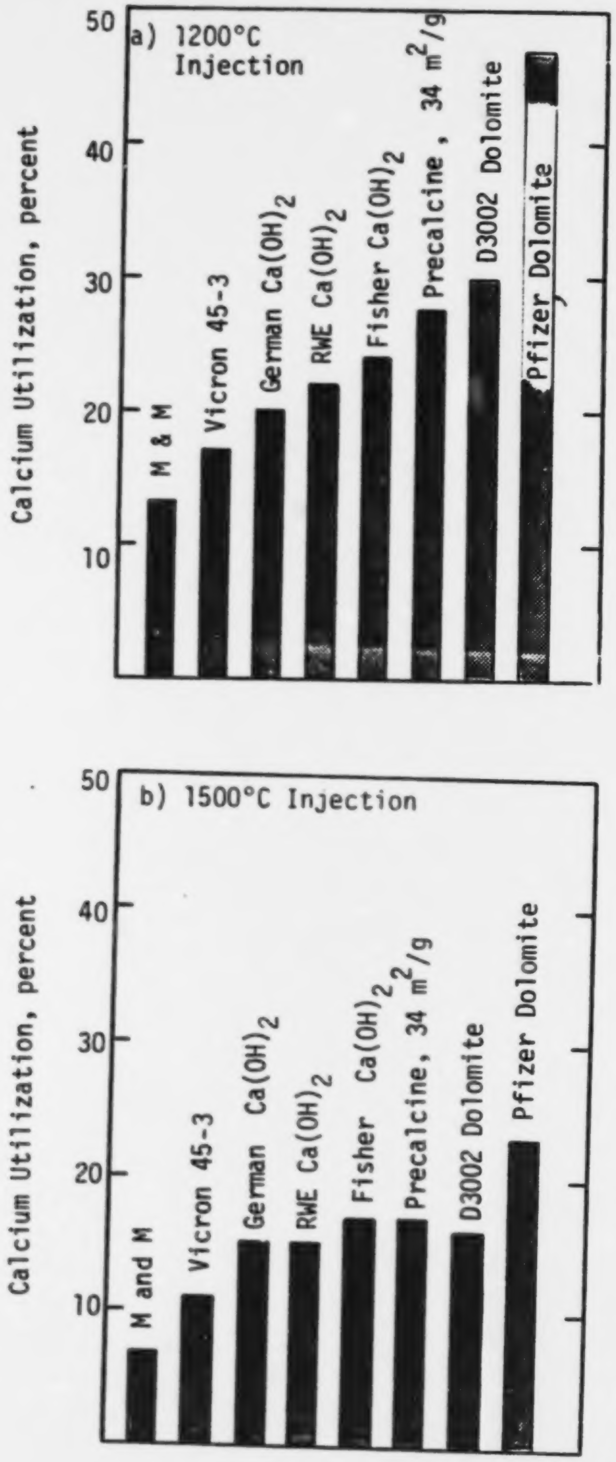

Figure 5. Reactivity ranking of eight sorbents injected into the thermal decomposition reactor at 1200 and 1500°C. Sulfation zone (reactivity probe) conditions were 1100°C, 0.6 s, 6% SO_2.

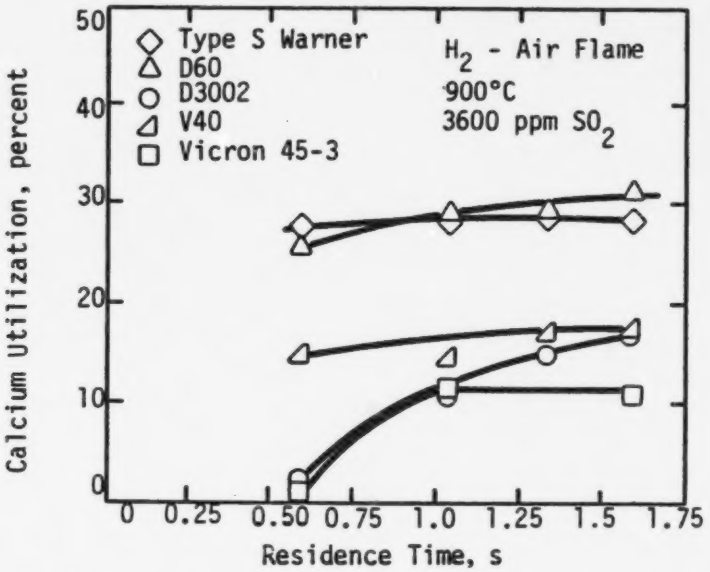

Figure 6. Calcium utilization profiles for five sorbents at 900°C.

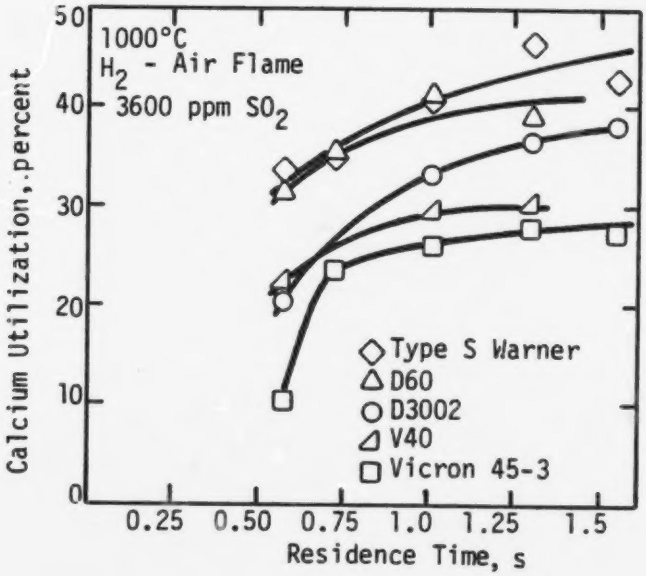

Figure 7. Calcium utilization profiles for five sorbents at 1000°C, 3600 ppm SO_2.

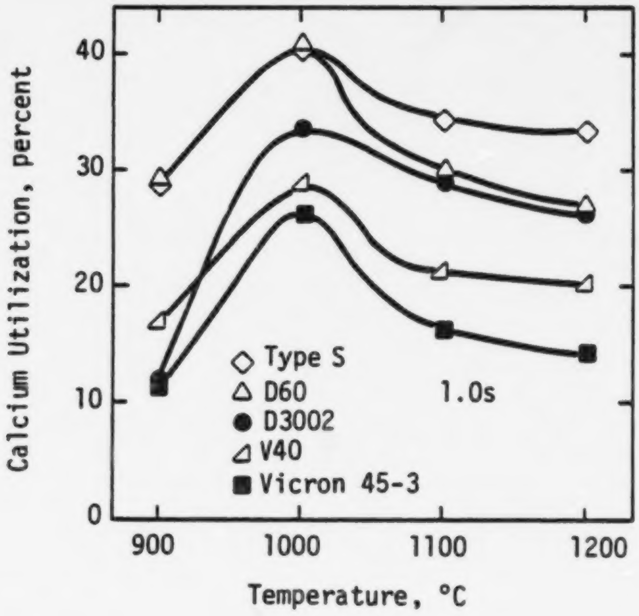

Figure 8. Relative levels of calcium utilization at 1.0s by five sorbents as a function of isothermal reaction/calcination temperature.

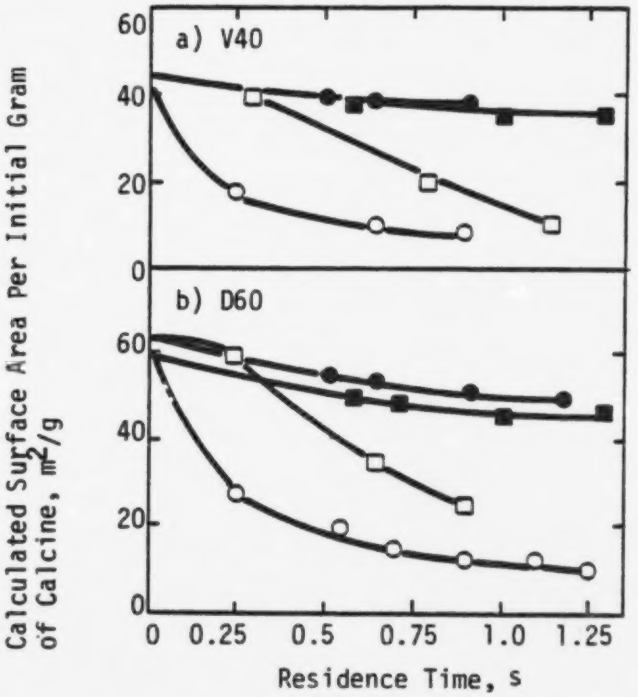

Figure 9. Change in specific surface area of a) V40 and b) D60 during sulfation in the ITR at □/■-1000°C and ○/● -1100°C. Open symbols represent the surface area required by the model to predict the data. Closed symbols represent the calculated loss of total surface area due to sulfation in the absence of sintering.

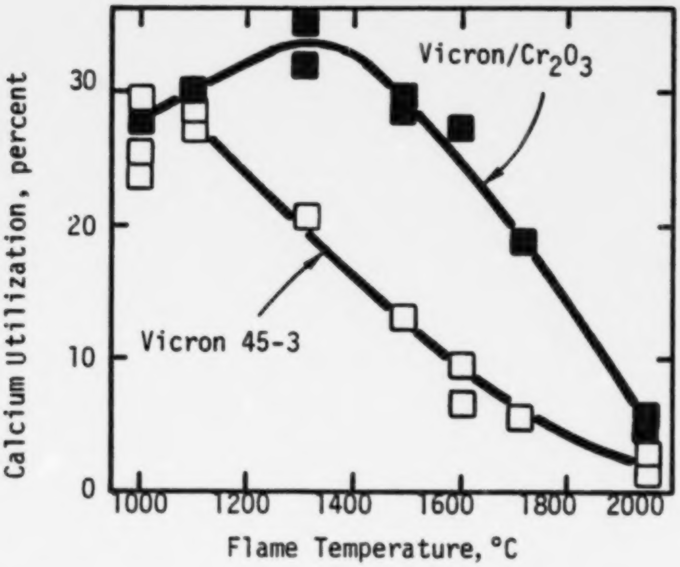

Figure 10. Calcium utilization of Vicron 45-3 with and without Cr_2O_3 as a function of initial flame temperature. 1100°C wall temperature, 3600 ppm SO_2.

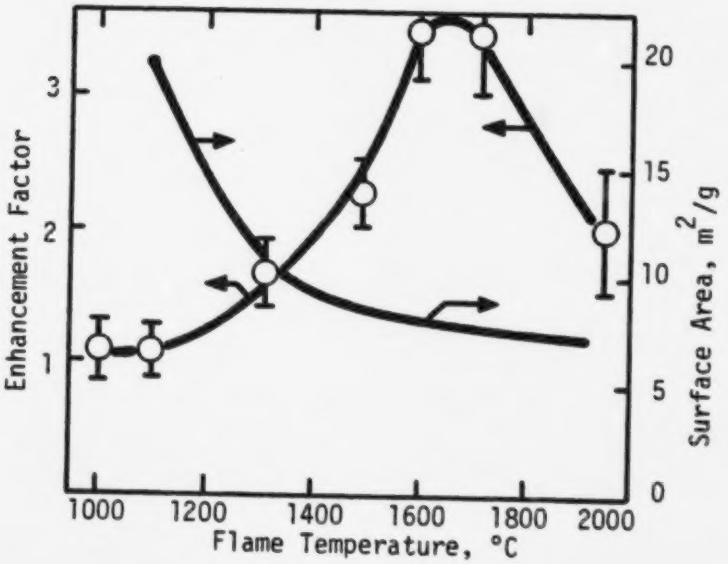

Figure 11. Ratio of calcium utilization with and without Cr_2O_3 by Vicron 45-3. Error bars signify one standard deviation. Also shown is the surface area measured for Vicron 45-3 as a function of peak calcination temperature.

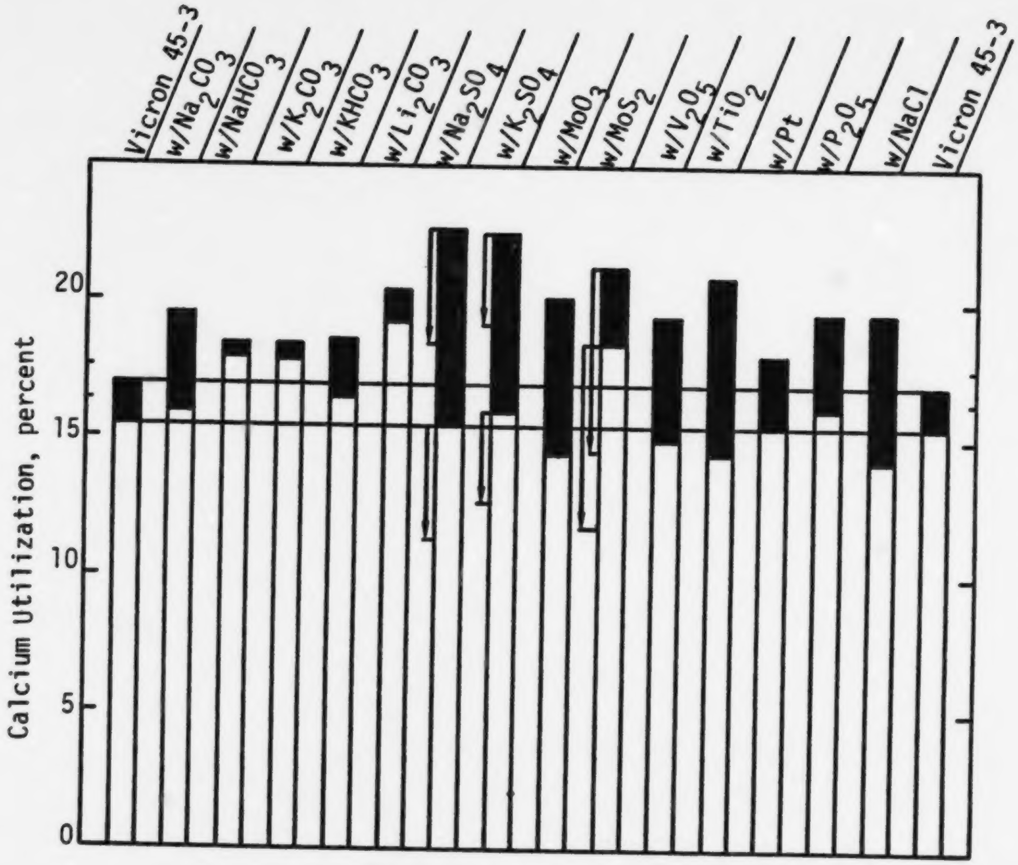

Figure 12. Calcium utilization by Vicron 45-3 in the presence of promoters under isothermal conditions in the ITR. 1100°C, 3600 ppm SO_2. The open portion of each bar presents utilization achieved in 0.92 s. The shaded portion shows the additional utilization at 1.4 s. For Li_2CO_3 the data at 0.92 s were higher than at 1.4 s. Arrows adjacent to Na_2SO_4 and MoS_2 designate the correction for the sulfur content of the additives.

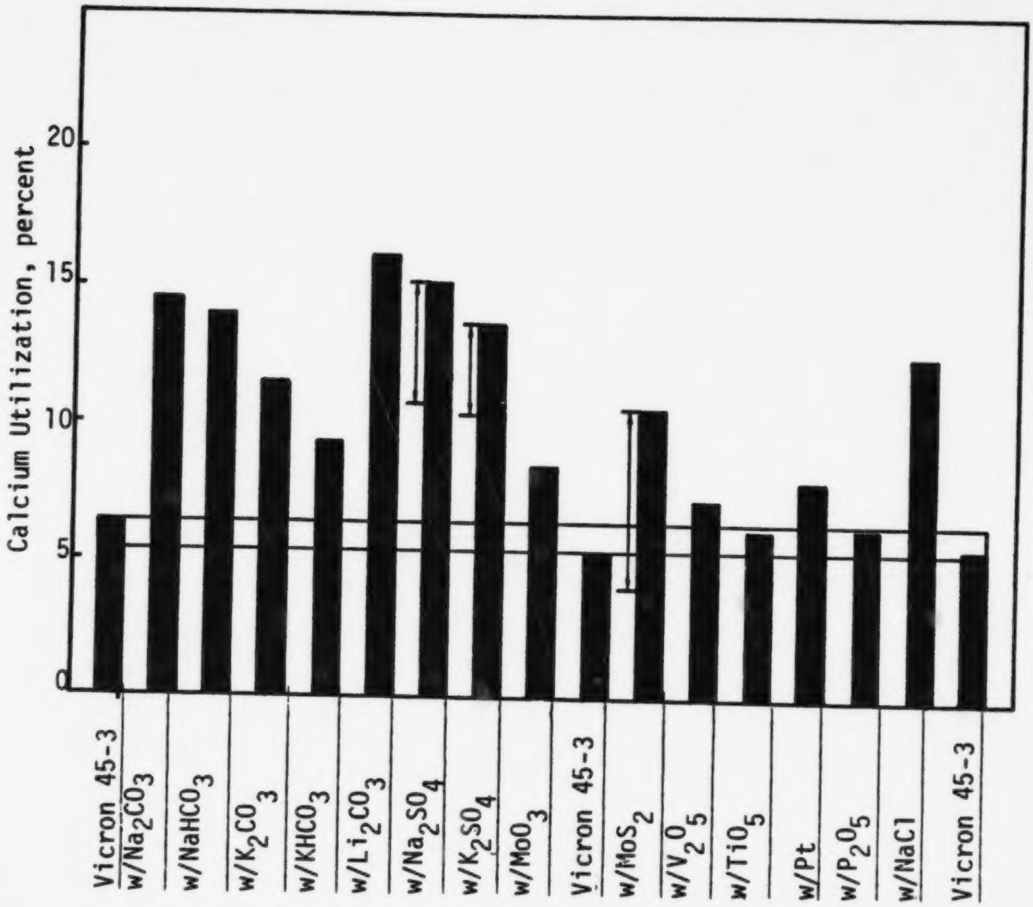

Figure 13. Calcium utilization by Vicron 45-3 in the presence of promoters in the ITR. Operating conditions: 3600 ppm SO_2, 1360°C CH_4/air flame, 1100°C wall temperature, 0.6 s residence time. The horizontal band shows the range of results obtained for Vicron 45-3 alone. Downward arrows adjacent to the data for Na_2SO_4, K_2SO_4, and MoS_2 indicate the correction for the original sulfur content of the additive.

BENCH SCALE EVALUATION OF SULFUR-SORBENT REACTIONS

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ABSTRACT

High temperature, isothermal data on calcination and SO_2 capture were obtained as a function of temperature, residence time, and Ca/S molar ratio for a wide variety of sorbents including limestones, dolomite, and slaked limes. The calcination results include extent of both calcination and surface area and define the relationship between thermal environment and sorbent characteristics. The experimental sulfation data indicate that sulfur capture is strongly dependent on the general class of sorbent. Reaction zone temperature was also found to critically influence the overall effectiveness of sulfur capture by sorbent injection; as the local temperature increases, the rate of heterogeneous chemical reaction and diffusion increase but they are ultimately compensated for by a decrease in initial sorbent surface area due to desurfacing during flash calcination. The results from the experimental studies are compared with theoretical predictions using a combined diffusion/heterogeneous chemical reaction model which was developed based on a grain formulation.

BACKGROUND

Introduction

Considerable attention is being focused on the control of SO_2 emissions from the combustion of sulfur-containing coals. The desire to reduce SO_2 emissions stems partly from their suspected role in acid rain formation. The addition of pulverized, dry, calcium-containing sorbents that react with SO_2 in the boiler or furnace to produce a solid product is potentially an economically attractive control method. The overall reaction associated with this process under oxidizing conditions is:

$$CaO + SO_2 + \frac{1}{2} O_2 = CaSO_4 \qquad (1)$$

Extensive early investigations of this control technique(1-4) defined the overall characteristics of the process, but yielded some conflicting and inconclusive results as to its effectiveness. These studies made clear the need for additional high temperature calcination and sulfation data with well-characterized sorbent particles.

The elementary reactions involved in the process represented by Equation (1) are unknown. Previous experimental studies(2) have indicated a weak dependence on oxygen concentration. The effect of SO_2 concentration is complicated by the presence of coupled diffusion and heterogeneous reaction steps; apparent orders of one(5), one-half(2), and zero(6) have been reported.

Purpose and Scope

The overall objective of the present study was to obtain high temperature sulfur capture data under conditions where the thermal environment and the sorbent properties were well-characterized. A 65 kW refractory-walled reactor was used to obtain isothermal capture data as a function of temperature for calcitic and dolomitic sorbents in both carbonate and hydroxide forms. The results of these experiments were compared to a grain model which included pore and product layer diffusion as well as heterogeneous chemical reaction. Sulfation kinetics were assumed to be zero order with respect to SO_2.

EXPERIMENTAL SYSTEMS

The isothermal reactor which was used to obtain the calcination and sulfation data is illustrated in Figure 1. The refractory-walled chamber is 3.0 m high with an inside diameter of 15 cm. The main natural-gas-fired burner is attached to the horizontal extension at the bottom of the furnace. This 65 kW burner supplies the hot combustion products which flow vertically upward within the reactor. An independent wall and gas temperature control is provided by a pair of 30 kW natural-gas auxiliary burners which are attached to the upper portion of the furnace and fired downward in annular channels around the main combustion chamber. All natural-gas and air streams supplied to the furnace are precisely metered with high accuracy rotameters. SO_2 is metered into the inlet gas stream to allow independent control of sulfur partial pressure.

The sorbent was metered with a K-tron twin-screw auger feeder, and was transported through an eductor to a water-cooled sorbent injector located at the bottom of the vertical reaction zone. A "showerhead" injector design was used to ensure rapid mixing of the sorbent with the combustion gas stream; both cold flow visualization and hot tracer studies were used to verify the extent of mixing.

The furnace exhaust was continuously monitored for CO, CO_2, O_2, and NO. SO_2 concentrations were continuously determined by withdrawing a gas sample through a controlled temperature, stainless steel, phase discrimination probe and pumping it to a DuPont UV 400 Photometric analyzer. Sample conditioning prior to the instrumentation consisted of two glass-wool filters, an electrically heated line to maintain the sample at 130° C, two Perma-pure dryers to selectively remove water from the flue gas, and a 60 µm, stainless steel filter.

Solid sorbent samples for subsequent surface area analysis were collected with a stainless steel, controlled temperature probe followed immediately by a high temperature filter. During the sampling, all parts of the system were maintained above 230° C to minimize hydration. At the conclusion of the sampling sequence, N_2 was forced through the system until the filter temperature was reduced to ambient and all samples were stored under nitrogen. Both the phase discrimination SO_2 probe and the solids collection probe were located at the top of the furnace just above the end of the controlled temperature zone and parallel to the flow.

MATHEMATICAL MODELING OF THE SO_2-LIME REACTION

The SO_2-lime reaction is a fluid-solid system which can be analyzed by assuming that the gaseous reactant, SO_2, must undergo the following:

- diffusion from the bulk gas to the particle's surface;
- pore diffusion to the particle's interior;
- solid state diffusion through the product layer ($CaSO_4$); and
- reaction at the product/lime interface.

A grain model formulation was adopted for this study based on high resolution STEM photographs of calcined dolomite particles which showed a grain-like structure with 100Å cracks. The modeling of the sulfation reaction by Hartman and Coughlin(7) for fluidized beds was used as a starting point. This model is based on the assumption that porous lime particles can be represented as conglomerates of nonporous spherical grains of pure CaO. Note that the major constituents of dolomite are $CaCO_3$ and $MgCO_3$. Dolomite calcines to form CaO and MgO. In this study, the $MgCO_3$ was also assumed to form spherical grains of pure MgO.

The reaction of the CaO grains with SO_2 was assumed to occur by the shrinking core model. The MgO does not react under the conditions of this study. Because of the differences in the molar volumes of pure CaO and $CaSO_4$ (17 and 46 cm^3 $gmol^{-1}$, respectively), the sulfation reaction necessarily involves the growth of the grains and the concomitant decrease in the porosity of the particle.

The following assumptions were made in the development of the grain model:

- the lime particles are fully calcined;
- the grains of CaO and MgO are of the same average size;
- the diffusion of reactant to the particle surface is not rate limiting;
- Equation (1) is irreversible and zero order with respect to SO_2;
- the sole reaction product is $CaSO_4$;
- the CaO grains react by the shrinking core model, and the MgO grains do not react; and
- excess oxygen is present.

The last assumption allows any reaction rate dependence on oxygen to be included as a constant in the rate term. The details of the overall mathematical formulation and numerical solution procedure have been described elsewhere(8).

DISCUSSION OF EXPERIMENTAL RESULTS

Sorbent Activation

Prior to the sulfation experiments, studies were conducted to establish the influence of reaction zone residence time and temperature on the calcination and subsequent activity of the sorbent materials. Each dry sorbent was injected at the beginning of the reaction zone (furnace bottom), and a solid sample was collected at the exit of the controlled temperature zone for subsequent surface area characterization. No SO_2 was present in these experiments; the surface areas reported are those associated with unreacted calcium oxide. Six sorbents were used in these and subsequent sulfation experiments: two high-purity large-grain limestones, two slaked limes, a 56% calcium carbonate dolomite, and a high-pressure slaked dolomite. Table 1 summarizes the chemical and physical properties of these materials prior to their introduction into the reactor.

Figure 2 summarizes the data obtained on surface area as a function of residence time within the reactor for the six sorbent materials. In these experiments the reactor temperature was maintained constant at 980° C ± 20° C (1800° F). (For the purposes of data reduction, the MgO and the CaO in the dolomitic materials were assumed to contribute surface areas based on their molar volumes and weight percentages.) As the calcination proceeded at 980° C with the limestones, the surface area developed rapidly; the initial increase occurred in less than 250 msec. The sorbents were more than 60% calcined at the first sampling point. The Vicron limestone exhibited a definite peak in surface area at approximately 300 msec and then the surface area decayed slightly. No obvious peak was observed with the Rollovit limestone.

Figure 2-B shows similar results for two slaked lime materials. These calcitic hydroxides began with much higher initial surface areas and were approximately 80% dehydrated by the first sampling point. A local maximum in surface area could exist within the first 200 msec; however, it was not possible to observe this behavior due to the limitations of the experimental apparatus. In general the slaked limes exhibited relatively little change in surface area, even at residence times up to 750 msec at 980° C. In fact, the only major difference between the calcitic carbonates and hydroxides was in initial surface area; after approximately 500 msec both the extent of calcination and surface area were very similar for all four of these materials (Figures 2-A and B).

Figure 2-C shows similar results with the dolomitic materials (both the natural dolomite, $CaCO_3.MgCO_3$ and the pressure-slaked dolomite, $Ca(OH)_2.Mg(OH)_2$). As in the case of the calcitic materials, the slaked dolomite began with a much higher initial surface area and exhibited a definite peak in surface area at approximately 300 msec. However, beyond approximately 500 msec the properties of both dolomitic materials appear to be very similar.

Figure 3 summarizes the data which were obtained for all six sorbents on surface area as a function of reactor temperature for constant reactor residence time of 460 msec. Figure 3-A shows the results for the two limestone sorbents and indicates that, while there are subtle differences between the sorbents, both stones behaved quite similarly. After 460 msec at 770° C calcination was less than 20% complete and the surface area had only begun to develop. By 870° C the calcination was approximately 60% complete and the surface area of both sorbents had reached nearly 30 m^2/g. Further increases in the reactor temperature resulted in ultimate decreases in the surface area at the 460 msec sampling point. At temperatures typical of large utility boiler injection schemes (2200° F) the surface area for these limestones would be approximately 10 to 20 m^2/g once the materials were fully calcined.

Figure 3-B shows similar data for the calcium hydroxides and indicates that, as in the case of the residence time studies, surface area is only weakly dependent on temperature. This may be because dehydration occurs extremely rapidly and all of the data shown in Figure 3-B represent essentially fully dehydrated particles; even at 770° C more than 70% of the material was dehydrated at 460 msec. Figure 3-B also shows that both hydroxides behave very similarly with respect to the influence of temperature.

Data for the dolomitic sorbents are shown in Figure 3-C. The surface areas for the pressure-slaked dolomite were large at all conditions; calcination at 870° C produced a peak surface area of nearly 50 m^2/g, a reasonably high value for dolomite which had been flash calcined in combustion gases. Further increases in reactor temperature resulted in a significant decrease in the available surface area. Beyond approximately 1000° C the pressure-slaked dolomite became essentially indistinguishable from the naturally occurring carbonate by the 460 msec sampling point (in terms of surface area). Physical inspection under the STEM did, however, indicate that the materials had retained their large initial difference in particle size; the pressure-slaked sorbent appeared to have a mean particle size less than 1 µm, while the natural occurring dolomite had a mean particle size of 20 µm.

In summary, the sorbent activation studies suggest that for each sorbent there exists an optimum reactor residence time and peak temperature for maximum surface area during flash calcination. There appear to be subtle differences between sorbent within the same class (ie. calcitic carbonates); however, the major differences occur between classes and in general dolomitic materials which produce higher surface areas than calcitic materials. In general hydrated sorbents produce higher surface areas under conditions where the calcination times are very limited, but beyond approximately 500 msec there does not appear to be a great difference between limestones and slaked limes.

Sulfation

Figure 4 shows the SO_2 capture as a function of reactor temperature over the same temperature range as the calcination studies for a calcium-to-sulfur ratio of 2.0 and a gas-phase SO_2 concentration (dry) of 2700 ppm. These data indicate that captures slightly in excess of 20% were achieved with the limestone sorbent (Vicron) in 460 msec. As reaction zone temperature was increased, the overall capture decreased dramatically. The solid line in Figures 4 shows the predictions made with the grain model using the measured thermal conditions and the measured surface areas. A 5 µm mean particle size was assumed for the limestone based on measurements of flash-calcined Vicron by Seeker and Cole(9). No adjustments were made to improve the agreement between the experimental results and the model predictions; all of the diffusion coefficients and kinetic rates were based on the prior fundamental work of Borgwardt(5). In general the grain model appears to be capable of approximately predicting the actual measured performance based on elementary kinetic measurements.

The overall trend shown in Figure 4, decreasing SO_2 capture with increasing reaction zone temperature, is almost certainly the result of a competition between sorbent desurfacing (sintering) which reduces the sites available for reaction with SO_2 and the diffusion surface reaction mechanism of the sulfation process. Figure 5-A shows a summary of the available data regarding the effect of reaction zone temperature on the surface area of flash-calcined Vicron in bench-scale combustion environments. This figure demonstrates that the results obtained in this work are consistent with those obtained by previous investigators and that the surface area available for reaction with SO_2 decreases dramatically as the peak calcination temperature is increased. Figure 5-B shows model predictions at a constant surface area of 15 m^2/g and indicates that, were surface area not a strong function of reactor temperature, sulfation would greatly increase with increasing temperature due to both increased pore and product layer diffusion and increased chemical reaction rates. It is the competition between these processes that produces the overall thermal effect shown in Figure 4, and the model does approximate these effects correctly.

It should also be noted that in the practical system a more favorable thermal environment (lower temperature) can be achieved by injecting the sorbent farther downstream from the burner zone; however, in actual field hardware there is an additional penalty associated with this because of a decreased downstream residence time. Unlike the idealized experiments illustrated in Figure 4, calcination temperature and sulfation zone residence time are not independent in a practical system.

Figure 6 summarizes the data obtained on the influence of reactor temperature for all six of the sorbents. These data were all obtained with a sulfation zone residence time of 460 msec and a gas-phase SO_2 concentration of 2700 ppm. The results are reported in terms of percent calcium utilization; in the case of the dolomitic material, the magnesium was assumed to remain unreacted based on early fundamental studies and recent work by Overmoe et al.(10). In general all of the calcitic materials (both the carbonates and the hydroxides) exhibited the temperature dependence previously discussed for the Vicron limestone; as the reactor temperature increased, the overall SO_2 capture decreased. For this relatively short sulfation zone residence time the peak calcium utilizations were between 10 and 20%.

In general the dolomitic materials exhibited much higher calcium utilizations. At both temperatures tested, the pressure-slaked dolomitic lime from Genstar produced calcium utilizations of approximately 35% (which would correspond to 70% SO_2 capture at a calcium-to-sulfur ratio of 2.0). These materials also appeared to be less temperature sensitive than their calcitic analogues. This effect is almost certainly due to the presence of the magnesium in the crystal structure and may relate to the prevention of pore closure.

Figure 7 shows a composite plot of calcium utilization as a function of surface area for the case with 460 msec residence time at 1090° C. This figure indicates that in general the higher calcium utilizations (higher SO_2 captures) are associated with an increase in sorbent surface area. These data also indicate that other factors (e.g. in situ particle size distribution, pore size distribution) are of some importance in terms of SO_2 capture by dry sorbent injection. Additional work is needed to clarify the role of these secondary effects.

CONCLUSIONS

The results of this study suggest that the fundamental sulfation data obtained by Borgwardt can be extrapolated to combustion conditions typical of pulverized coal boilers and used in conjunction with an appropriate diffusion/heterogeneous chemical kinetic model to predict SO_2 capture by dry sorbent materials. Temperature in the reaction zone was found to have a critical influence on SO_2 capture because it controls the reactivity of the sorbent (as characterized primarily by the surface area) and the overall rates of diffusion and heterogeneous reaction. Increasing termperature increases both the kinetic and diffusion rates; however, it significantly decreases the surface area of the sorbent at the end of the flash calcination process and, thereby, reduces the sites available for reaction with SO_2.

As expected, dehydration of slaked limes occurs significantly more rapidly than calcination of carbonates, but beyond approximately 500 msec at 900° C the surface areas of all the calcitic materials used in this investigation were similar. In general both the dolomitic carbonate and the dolomitic hydroxide produced significantly higher surface areas at all conditions tested, and this resulted in overall higher SO_2 captures for these materials. Calcium utilizations in excess of 35% can be achieved in less than 500 msec with pressure-slaked dolomitic sorbents.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of Robert H. Borgwardt, G. Blair Martin, Dennis C. Drehmel, and David A. Kirchgessner of the U.S. Environmental Protection Agency and P. L. Case, W. R. Seeker, and M. P. Heap of the Energy and Environmental Research Corporation. This work was completed under EPA Cooperative Agreement CR-811001.

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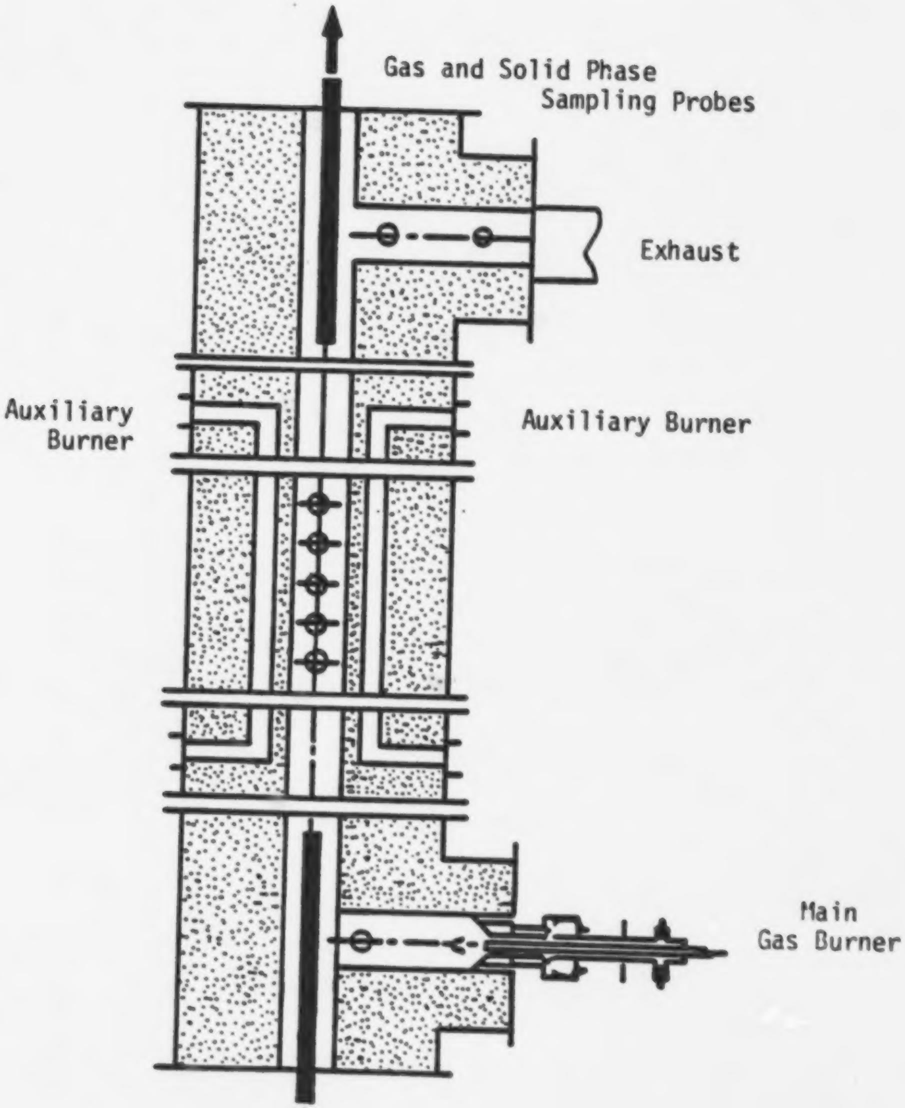
Gas and Solid Phase Sampling Probes
Exhaust
Auxiliary Burner
Auxiliary Burner
Main Gas Burner
Sorbent Injector

Figure 1. Schematic of Isothermal Reactor

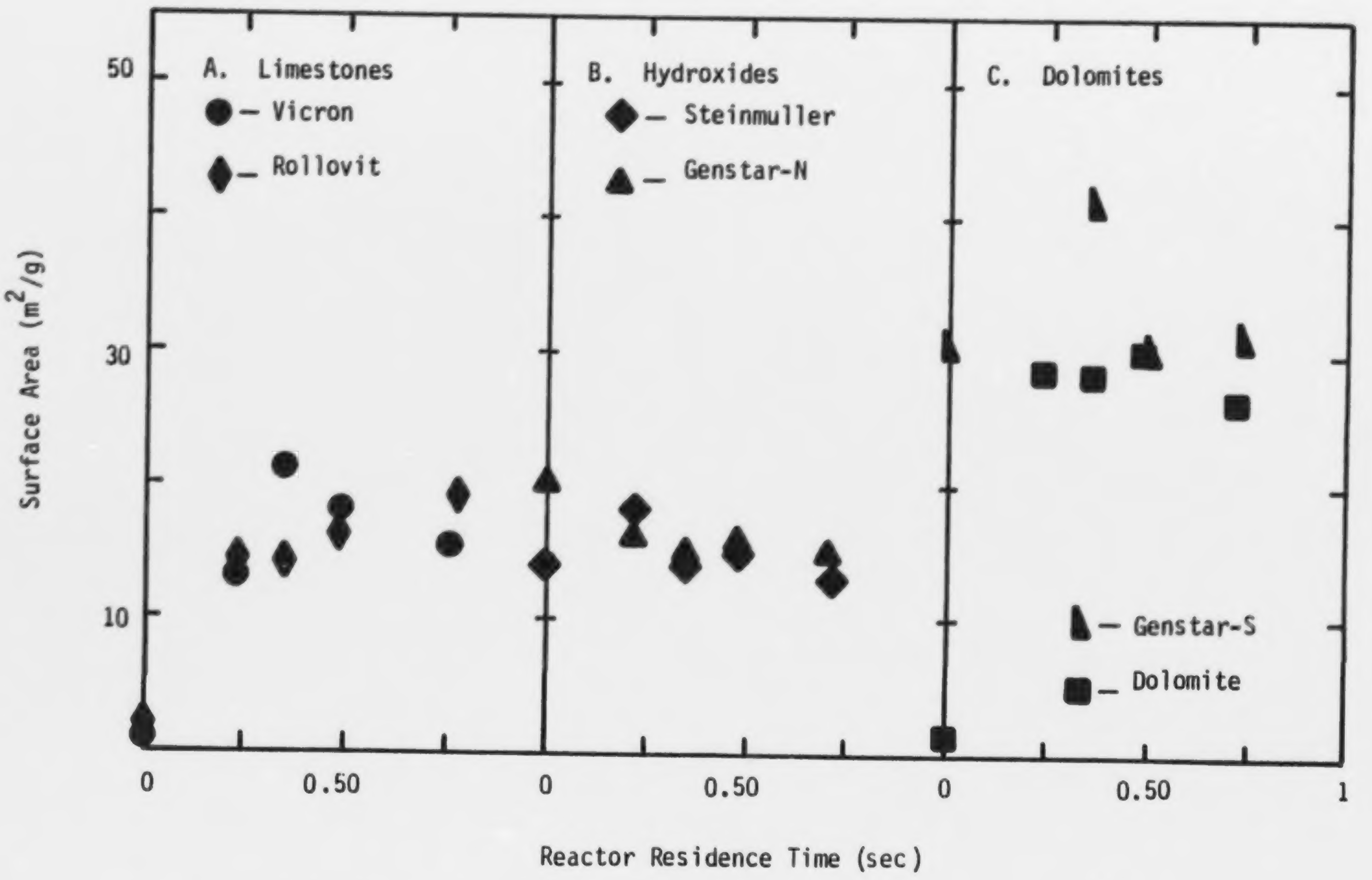

Figure 2. Development of Surface Area at 980°C (1800°F).

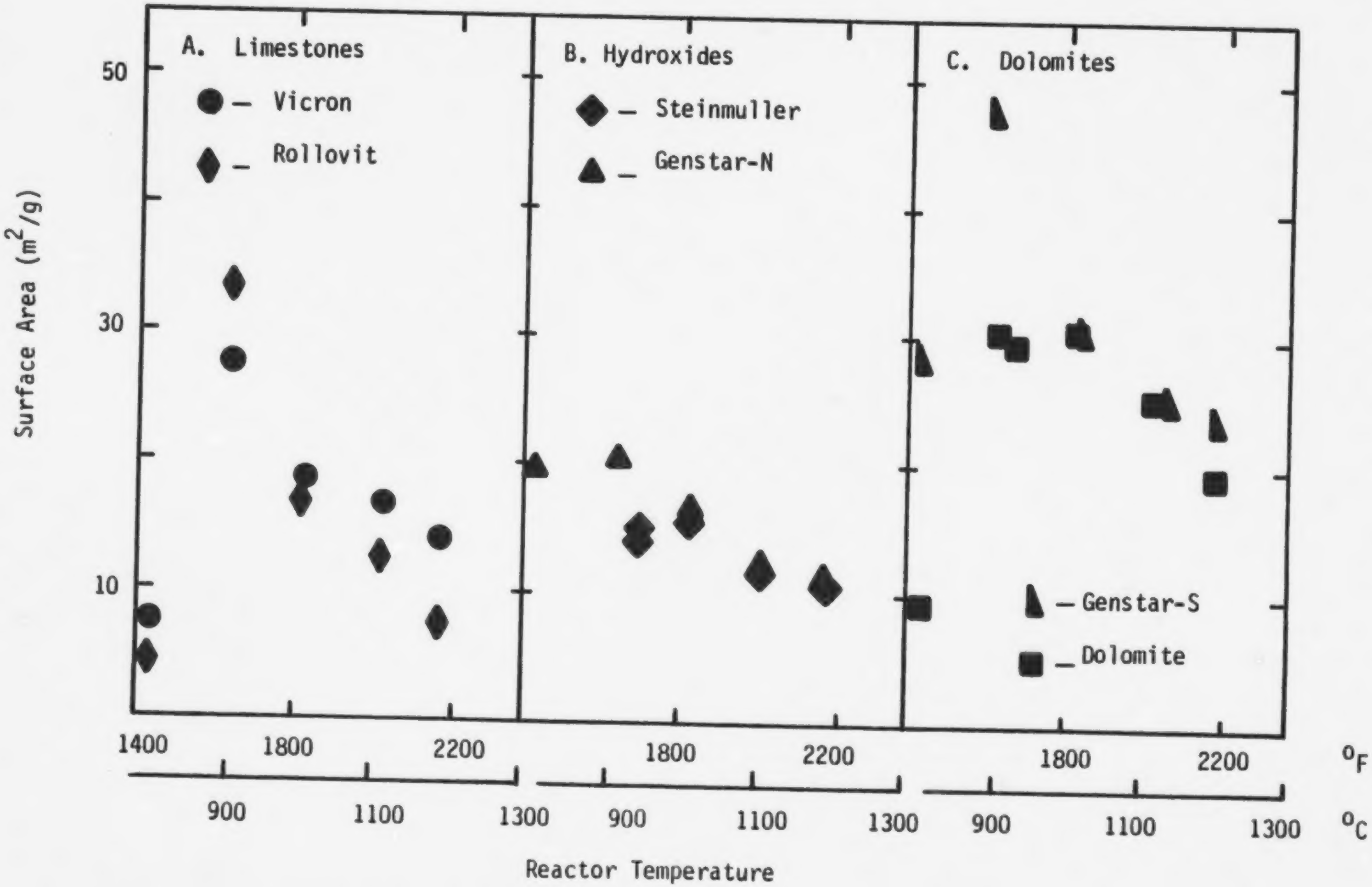

Figure 3. Influence of Calcination Temperature on Surface Area Development (460 ms residence time).

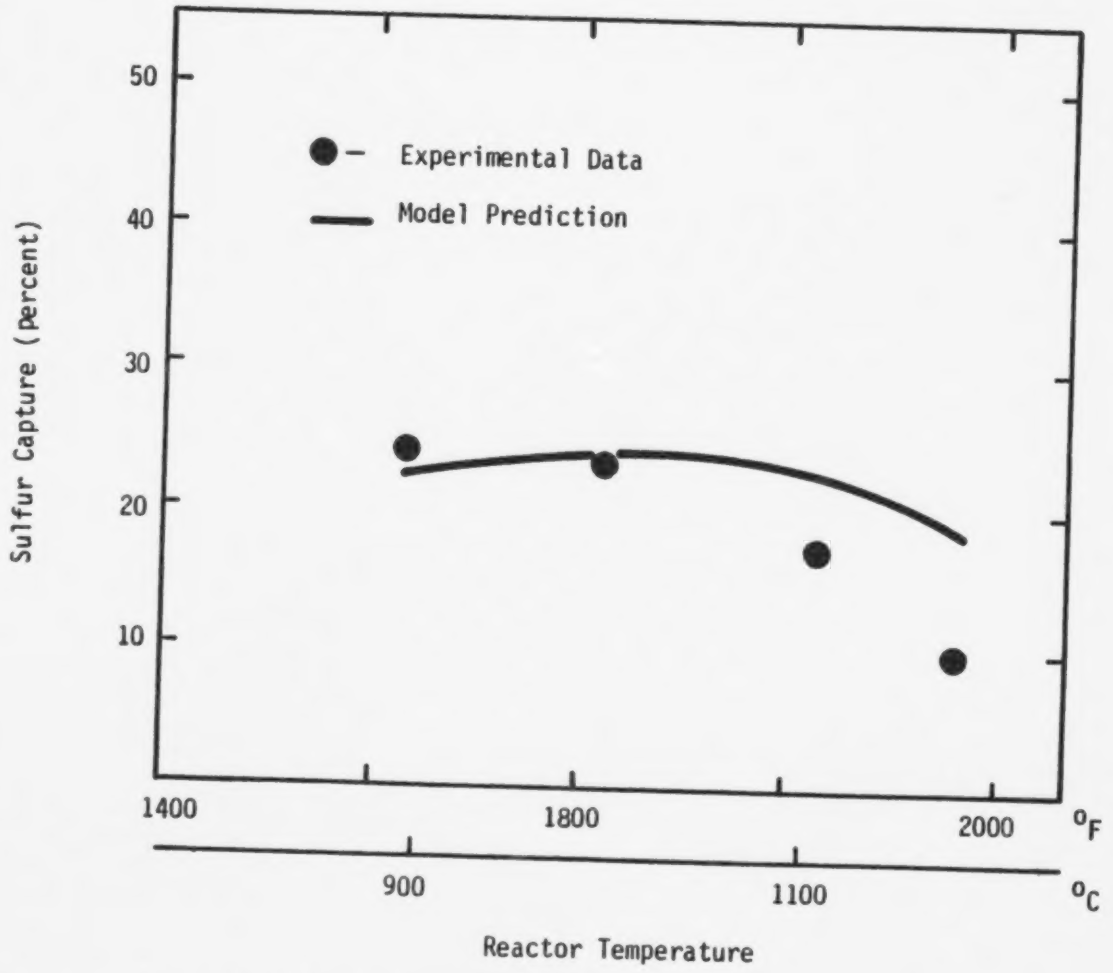

Figure 4. Sulfur Capture: Comparison of Theory and Experiment ($Ca/S = 2.0$, $SO_2 = 2700$ ppm, Residence Time = 460 ms)

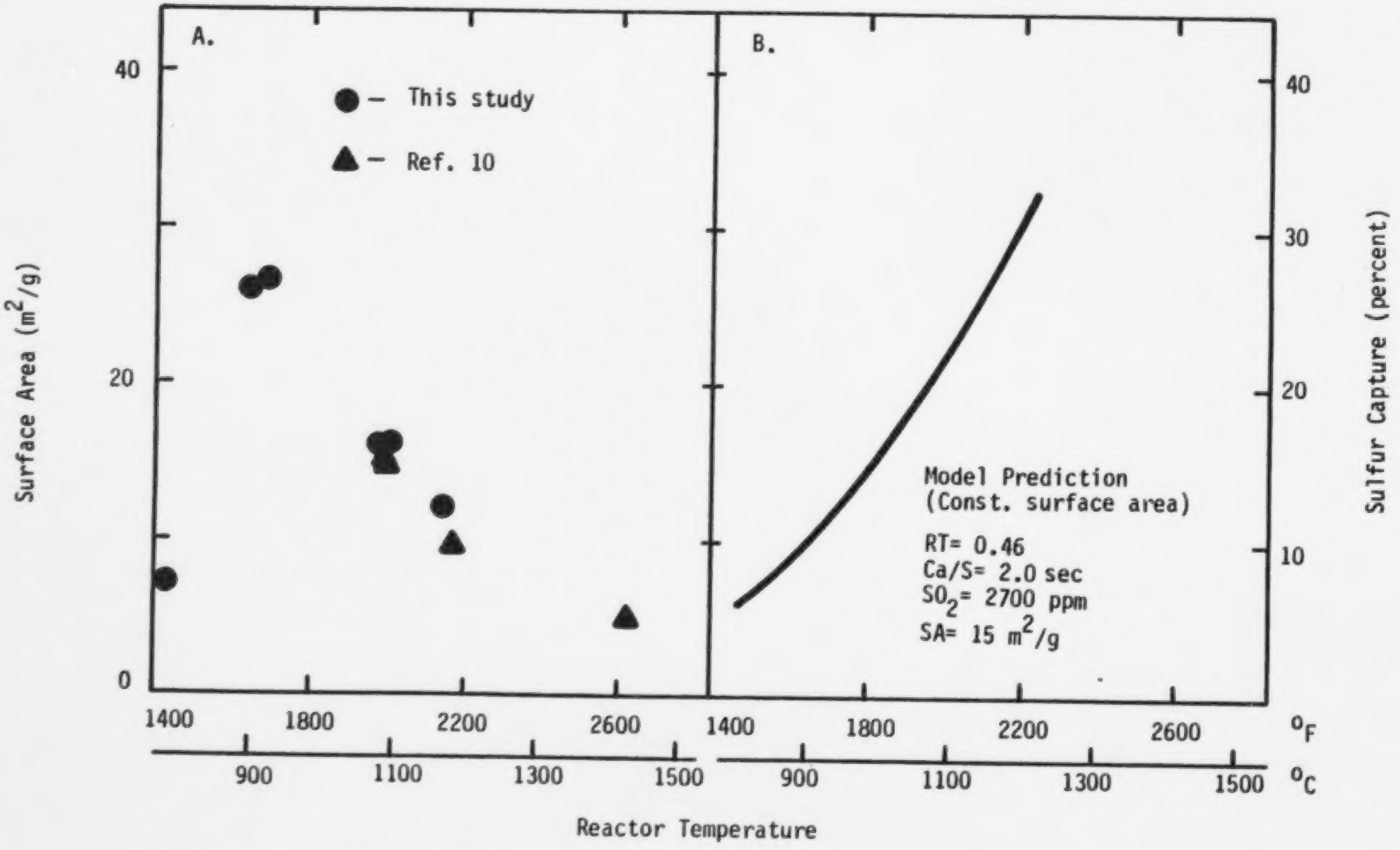

Figure 5. Individual Effects of Thermal History (Vicron)

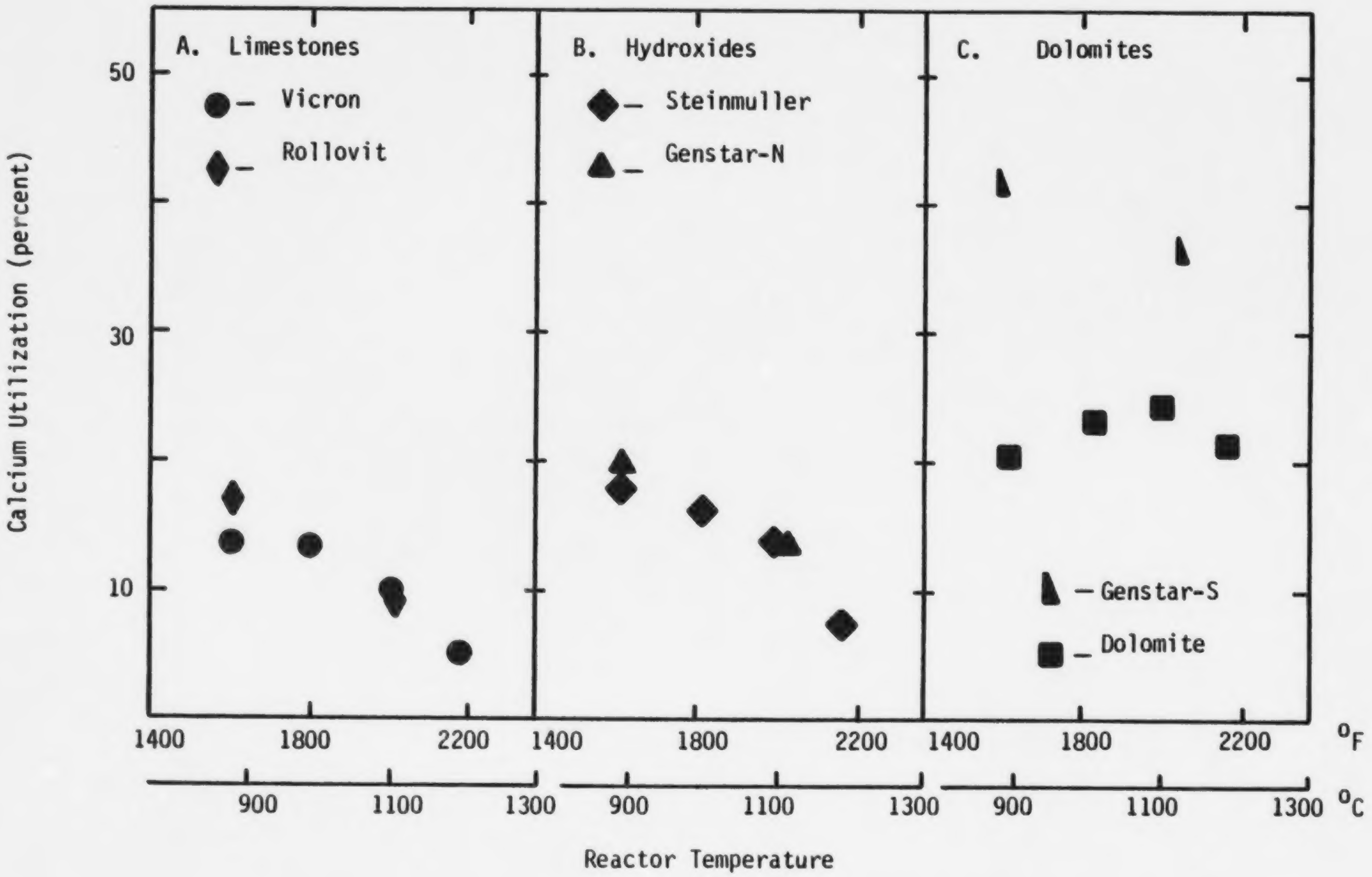

Figure 6. Influence of Thermal Environment on Calcium Utilization (SO_2 = 2700 ppm, Residence Time = 460 ms)

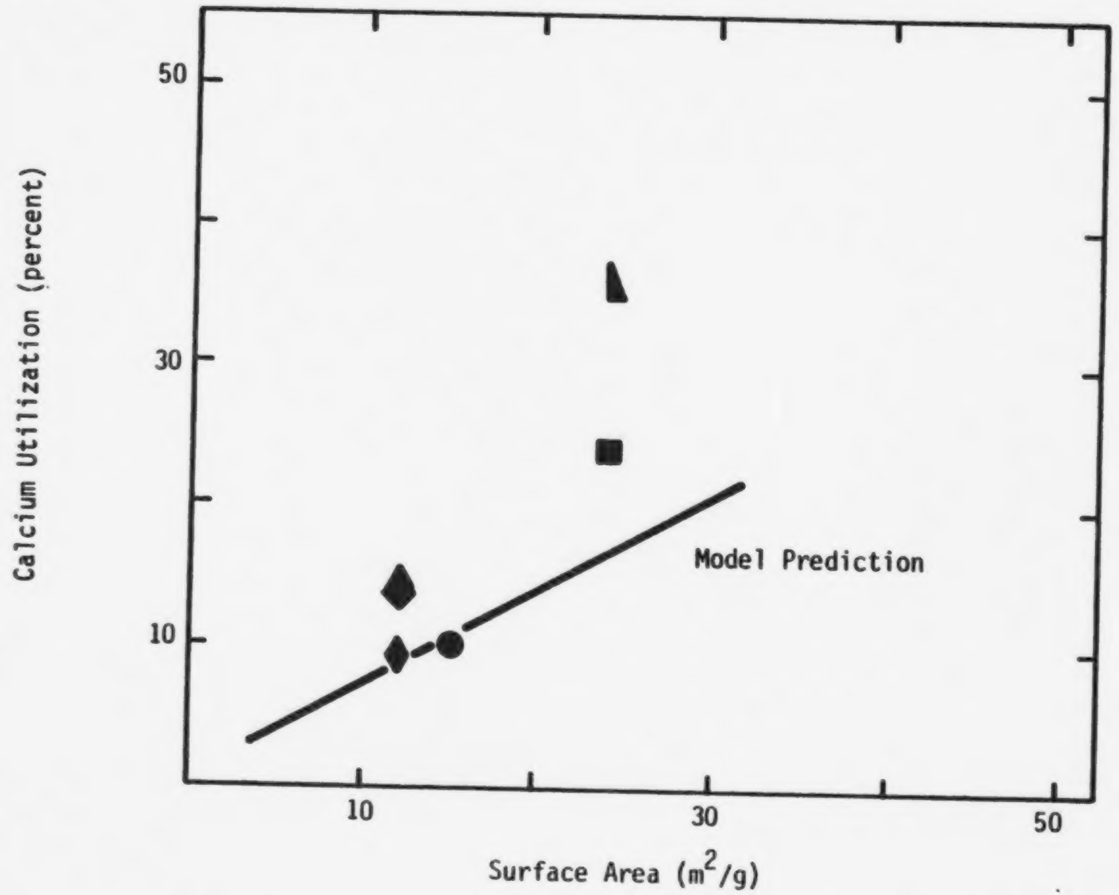

Figure 7. Correlation of Calcium Utilization With Surface Area (SO_2 = 2700 ppm, Temperature = 1090°C = 2000°F, Residence Time = 460 ms)

TABLE 1. SORBENT CHARACTERISTICS

Sorbent	Dolomite	Genstar-S	Genstar-N	SM $Ca(OH)_2$	Vicron 45-3	Rollovit
Type	Dolomite	Dolomitic Pressurized Hydrated Lime	Hydrated Lime	Hydrated Lime	Calcite	Chalk
Composition	$CaCO_3$ $MgCO_3$	$Ca(OH)_2$ $Mg(OH)_2$	$Ca(OH)_2$	$Ca(OH)_2$	$CaCO_3$	$CaCO_3$
Top Size, µm	<100		30	30	45,40	<40
Mean Size, µm	34.0,40	1.4	3.0	3.5	11,12	6
Bottom Size, µm	1.0			0.3	0.3,0.8	
Density, g/cm^3	2.855	2.28	2.30	2.35	2.757	2.37
Initial Surface Area, m^2/g	0.64,0.60	30	20	13.5,12.1	0.9,0.6	1.73
Surface Area at 1000° C, m^2/g	47.1,44.2			25.3	44.0,41.0	43.8
Ca, %	21.0	29		51.0	39.2	37
Mg, %	12.1	16			0.485	0.50

EVALUATION OF SO_2 REMOVAL BY FURNACE LIMESTONE INJECTION WITH TANGENTIALLY FIRED LOW-NO_x BURNER

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ABSTRACT

The Mitsubishi Heavy Industries (MHI) contracted with the Electric Power Research Institute (EPRI) and Electric Power Development Company (EPDC, Japan) to evaluate the SO_2-removal effectiveness of furnace limestone injection when applied in combination with a low-NOx burner.

The evaluation included a series of furnace limestone injection tests conducted at MHI's 4 ton/hour pulverized coal-fired test furnace equipped with the low-NOx PM burner developed by MHI. The results showed 30 to 40 percent reduction of SO_2 at a Ca/S molar ratio of 2:1 while maintaining low-NOx combustion conditions compatible with full-scale utility boilers and operating practices.

Basic (bench-scale) tests were carried out prior to the combustion tests, using an electrically heated flow reactor. The resutls from the basic tests were applied in interpreting the results from the combustion tests.

EVALUATION OF SO_2 REMOVAL BY FURNACE LIMESTONE INJECTION WITH TANGENTIALLY FIRED LOW-NO_x BURNER

INTRODUCTION

The growing problem of atmospheric pollution by nitrogen oxides (NOx) and sulfur oxides (SOx) in stack gases of pulverized coal-fired power plants has generated a large amount of research and development activity aimed at demonstraiting suitable emission reduction technologies.

Of the several processes that could decrease the NOx and SOx emissions, the injection of limestone or other calcuim compounds into furnaces equipped with low-NOx burners is simplest and requires the least investment.

In this process, SO_2 reacts with limestone within the furnace to form solid sulfate particles which are then removed from the flue gas in the conventional particulate control device.

This paper shows the results of the experimental evaluation of SO_2 removal by furnace limestone injection when applied in combination with the low-NOx PM burner technology (1), (2), (3). The evaluation centered around tests at the MHI's 4 ton/hour combustion test furnace (nominally 12.5 MW) which is designed to maintain combustion conditions comparable to full-scale utility boilers and operating practice.

SO_2 REMOVAL CHARACTERISTICS BY LIMESTONE WITH REACTOR TUBE TEST APPARATUS

Basic limestone injection research on additive type, composition, surface area, point of injection and Ca/S molar ratio was conducted in 1970's (4), (5), (6), (7), (8). Approximately 30 percent SO_2 reduction was achieved at the average Ca/S molar ratio of 1.5:1 (9). This work was followed by full-scale testing by the Tennessee Valley Authority [TVA] at their Shawnee Steam Plant (10). These studies indicated approximately 20 percent SO_2 capture at the Ca/S molar ratio of 2:1.

The general reaction describing sulfur capture under oxidizing condition shown in the following formula has been studied extensively by several researchers (11), (12).

$$CaO + SO_2 + \frac{1}{2} O_2 \rightarrow CaSO_4 \qquad (1\text{-}1)$$

However, none of these studies duplicated the time/temperature conditions that prevail in pulverized-coal flames. Borgwardt (13) has suggested that the reactions formulated in (1-2) and (1-3) could be significant under fuel-rich conditions.

$$CaCO_3 + H_2S \rightarrow CaS + H_2O + CO_2 \qquad (1\text{-}2)$$

$$CaO + H_2S \rightarrow CaS + H_2O \qquad (1\text{-}3)$$

Low NOx coal burners produce extensive fuel-rich regions in addition to the usual fuel-lean burnout regions of the flame. Consequently, there are two possible modes by which calcium-based sorbents may capture sulfur species in a pulverized coal-fired boiler operating under low NOx conditions.

In the fuel-lean region the reaction (1-1) may proceed because the lower peak temperature will minimize a loss of surface area (deadburning). In the fuel-rich region the formation of calcium sulfide may be significant.

However, Pershing (14) showed that sulfur capture should be enhanced under fuel-rich conditions but sulfur retention in the coal char and its regeneration during burnout could negate this benefit.

As reviewed above, there are some discrepancies in the opinions of different researchers. These may be due to the differences in the test equipment or test conditions employed.

To clarify sulfur capture mechanisms, basic data on process fundamentals was felt to be necessary. For this purpose the basic tests were performed.

Test Apparatus and Test Method

Fig. 1 shows the test apparatus used. The body of the test furnace is composed of two cylindrical electric furnaces vertically connected, and inside them are located two ceramic reactor tubes each 24 millimeters in diameter and 1000 millimeters in length connected end to end with a silica joint. The primary reactor (upper electric furnace) is for the reaction of limestone with SO_2, and the secondary reactor (lower electric furnace) is for the complete conversion of $CaCO_3$ to CO_2 at higher gas temperatures (>1400°C).

The quantity of limestone injected is calculated from the measured CO_2 concentration in the gas. Pulverized limestone with a prepared particle diameter of under 56 micro-meters (250 meshes) is stored in a vessel at the top of the apparatus and dropped into the top of the primary reactor with two vibrators.

Test Results and Discussions

For the presentation of the results the removal rate of SO_2 (ηSO_2) for a specific Ca/S molar ratio is defined as percent of inlet SO_2 removed.

Fig. 2-1, Fig. 2-2 and Fig. 2-3 show the effects of the Ca/S molar ratio, gas temperatures and residence time on the SO_2 removal rate, respectively.

These figures indicate the following:

(1) SO_2 removal efficiency increases with Ca/S molar ratios from 0.0 to 4.0, but begins to level off at Ca/S molar ratios larger than about 4.0.

(2) Optimum SO_2 removal conditions in the tunnel flow type furnace used is different from that found in a fluidized bed furnace. The optimum gas temperature in Fig. 2-2 is from 950 degrees to 1100 degrees centigrade. In case of SO_2 removal in fluidized bed combustion, the optimum gas temperature is from 850 degrees to 950 degrees centigrade. It could be considered that the difference in the optimum gas temperature between pulverized coal combustion and fluidized bed combustion is based on the great difference in limestone reaction time with SO_2.

(3) Maximum SO_2 removal efficiencies are 30 percent at the residence time of 0.54 seconds and 80 percent at that of 1.54 seconds respectively.

These test results show a qualitative agreement with the results from other pilot-scale and bench-scale tests (5), (6), (14).

Fig. 2-4 shows the effect of the limestone fineness on the SO_2 removal rate. The SO_2 removal rate at Ca/S molar ratio of 2.0 increased to 47 percent from 40 percent with increased fineness. From Fig. 2-4, the SO_2 removal rate is proportional to about one-third power of limestone fineness. Ishihara (7) showed that the reactivity of limestone was proportional to one-third to one-fourth power of limestone fineness. Ishihara's test result shows a quantitatively excellent agreement with that shown in Fig. 2-4.

Fig. 2-5 shows the effect of SO_2 inlet concentration on the SO_2 removal by limestone. The SO_2 removal rate is increased with the increment of sulfur content in combustion gases and is proportional to one-fifth to one-sixth power of sulfur content at 1.0 to 2.0 of Ca/S molar ratio. But, the value of power slightly changes with the Ca/S molar ratio, the residence time and so on. Meanwhile, Ishihara (7) showed that the reaction rate of limestone was proportional to 0.3 to 0.5 power of sulfur content. It would be possible to understand that the difference in the value of power is based on a different Ca/S molar ratio, residence time and reaction temperature.

As mentioned before, it was suggested that the SO_2 removal rate should be increased due to the reducing atmosphere in addition to lower combustion temperatures in low-NOx combustion condition (13). The reactivity of limestone with H_2S in the zero percent oxygen atmosphere was investigated, simulating the actual pulverized coal combustion with over fire air. Here, it was assumed that sulfur species in the reduced atmosphere was only H_2S with COS left out of consideration.

Fig. 2-6 shows the reactivity of H_2S with limestone in the zero percent oxygen atmosphere as compared with that of SO_2 in the oxidized atmosphere as shown in Fig. 2-1. Although the oxygen content in the reaction zone of H_2S with limestone was zero percent, the oxygen content at the inlet of the second reactor tube, where limestone was calcined perfectly, was kept constant at three percent by adding oxygen as over fire air for measuring the concentration of H_2S as SO_2. From Fig. 2-6, the reactivity of H_2S with limestone is around half of that of SO_2 in the oxidized atmosphere.

Fig. 2-7 shows the effect of the inlet gas composition on the SO_2 removal rate as compared with the result of the base condition shown in Fig. 2-1. It is clarified that the SO_2 removal rate of the inlet gas containing H_2, CO and zero percent oxygen is lower than that of the base condition.

Moreover, the SO_2 removal rate of the inlet gas containing one percent H_2 is about 40 percent with and/or without limestone. And, this reduction of SO_2 could be understood to suggest that SO_2 decomposes after its reaction with H_2 while solid sulfur is formed and sticks onto the inside surface of the reactor tube. Moreover, it means that the SO_2 removal by limestone is almost zero in the reduced atmosphere with H_2.

Fig. 2-8 shows the effect of methane contained in the inlet gas on the SO_2 removal rate. By addition of 1000 ppm of methane to the inlet gas, the SO_2 removal rate decreased slightly and there was no difference in the optimum gas temperature for the SO_2 removal.

Moreover, it was reported (15) that the SO_2 removal rate also decreased with the decrement of air ratio in the primary combustion zone in the fluidized bed boiler.

Since the SO_2 removal rate is considerably lowered in the reduced and/or zero percent oxygen atmosphere, as mentioned above, it is clarified that the reaction of limestone with sulfur species such as H_2S in the reduced atmosphere is not desirable to keep a high SO_2 removal rate.

ANALYSES OF COALS AND LIMESTONE TESTED

The two bituminous coals selected for the limestone injection test provide a wide range of sulfur contents. The results of analyses of the two coals are shown in Table 1.

The limestone of Japanese Ikura was selected for the limestone injection test as a high quality of $CaCO_3$. The result of analysis of the limestone is shown in Table 2.

Three values of limestone fineness were selected for the limestone injection tests. The finenesses are 80, 97 and 100 percent through 200 mesh.

FACILITIES FOR COMBUSTION TEST

Tangential Fired Low-NOx PM Burner

The low-NOx PM burner, which had been previously tested and verified (1), (2), (3), was selected as a suitable low-NOx burner for the limestone injection tests. The basic concept of this burner is as follows:

(1) Pulverized coal in the primary combustion zone (that is the combustion zone for volatile matter in coal) should be rapidly burned under stable and high temperature condition with an adequate residence time to give a low NOx level and good stability.

(2) The air/coal mixture to the burner should be divided into two streams, a coal-rich stream and a coal-lean stream, and be burned separately through different nozzles contained in the same burner.

(3) The coal-rich flame and coal-lean flame combined produce low NOx. The former has a good ignition stability and the latter essentially reduces unburned carbon in fly ash due to a high oxygen content.

(4) With the above, by combining coal-rich flame and coal-lean flame, pulverized coal can be burned stably and efficiently (with low unburned carbon) with an extremely low NOx emission level.

Fig. 3-1 shows the structure of a coal-fired low-NOx PM burner.

Combustion Test Equipment

Fig. 3-2 shows a flow sheet of the 4 ton/hour (nominally 12.5 MW) test furnace. The body of the furnace is a sea-water-cooled double-walled cylinder of 4.4 meters in inside diameter and 20 meters in length. A part of its inner surface is lined with refractory to keep the furnace temperature at around the level of the actual boiler furnace so that the flame ignition characteristics, the degree of NOx formation and the percentage of unburned carbon in fly ash in the actual boiler can be simulated.

Measuring Instruments

Measured items, measuring instruments and measuring method used are shown in Table 3.

Flue gas was sampled for analysis of SO_2 at the following locations: (1) along the furnace flame axis, (2) furnace outlet, (3) multicyclone outlet, (4) bag filter inlet and (5) bag filter outlet.

Fig. 3-2 also shows the location of SO_2 measuring point in the 4 ton/hour test furnace. Overall sulfur material balance has been calculated, based on the analyses of the solid and the gaseous sulfur samples at each section mentioned above.

TEST METHOD

The limestone injection conditions that were changed included the limestone-injecting method, the Ca/S molar ratio, the limestone fineness, the combustion rate and the oxygen content in the flue gas.

Moreover, the amount of over fire air (OFA, which was introduced downstream of the flame) and the amount of the recirculated gas flow through the "Shield" gas recirculation nozzle (SGR) were changed.

The burner primary air temperature and pulverized coal fineness remained constant at 80 degrees centigrade and 70 percent through 200 mesh, respectively.

Fig. 3-3 shows the various arrangements of injecting systems used for the pulverized coal and/or limestone. The type (a) shown in Fig. 3-3 is the coal/limestone mixing system. The primary air is led to below the pulverized coal bin and the limestone bin, and passes to the burner, carrying pulverized-coal and limestone fed through the coal feeder and the limestone feeder, respectively. Here, the pulverized coal and the limestone were well mixed by the exhaust fan.

The type (b) shown in Fig. 3-3 is the system through the auxiliary air nozzle. The pulverized-coal and limestone are separately transported to the burner from each bin. And, the limestone is injected into the furnace from the auxiliary air nozzle provided above the coal-rich coal nozzle.

The type (c) shown in Fig. 3-3 is the system through the OFA nozzle. In this system, the limestone is transported from the limestone bin to the OFA nozzle by the limestone primary air. And, the limestone is injected into the furnace from the three OFA nozzles provided around the furnace body after being mixed with the over fire air.

The type (d) shown in Fig. 3-3 is the system through the gas recirculation (GR) nozzle. In this system, the limestone is transported by the recirculated flue gas from the limestone bin to the GR nozzles located around the furnace body downstream of the OFA nozzle. The limestone is injected into the furnace from the three GR nozzles after being mixed with the recirculated flue gases.

TEST RESULTS

Optimum Limestone Injecting Method

Four types of the limestone injecting methods, as mentioned before, were tested with high sulfur coal. Here, the SO_2 removal rate is defined as percent reduction of the SO_2 gas concentration in flue gas compared to the value of that without limestone injection.

Fig. 4-1 shows the comparison of the SO_2 removal rates with each type of injecting method. Although the SO_2 removal rate increases with the Ca/S molar ratio in all types of injecting methods, there are great differences in the SO_2 removal rates with the same Ca/S molar ratio in the four types of injecting methods. It is clarified from Fig. 4-1 that the type (c), which is through the OFA nozzle system, is the most suitable system to remove SO_2 gases in the furnace.

Since the oxygen concentration of the type (c) in the reaction zone of SO_2 and CaO is highest due to the mixing of limestone with the total amount of over fire air and the SO_2 removal rate increases with the oxygen concentration in the reaction zone as mentioned before, it may be understood that the SO_2 removal rate of the type (c) shows the highest value in those of all types of injection methods.

SO_2 Removal Characteristics

The relation of SO_2 removal rates to limestone injection conditions and/or burner operating conditions are shown in Fig. 5-1 to Fig. 5-3.

Effect of Ca/S Molar Ratio on SO_2 Removal Rate. Fig. 5-1 shows the relation of the SO_2 removal rate to the Ca/S molar ratio with the high sulfur (HS) and the low sulfur (LS) content coals. These tests were made by changing the limestone flow rate only.

Although the SO_2 removal rate increases with the increment of the Ca/S molar ratio, this upturn rate gradually flattens with the further increment of the Ca/S molar ratio.

The SO_2 removal rate with HS coal is higher than that with LS coal. The SO_2 removal rate at a Ca/S molar ratio of 2.0 is 44 and 35 percent, respectively.

From these values of the SO_2 removal rates, the SO_2 removal rate is proportional to one-fifth power of the sulfur content in coal. And, the results of the basic information tests shown in Fig. 2-5 show a similar dependence on the sulfur content. Earlier studies have shown that the sulfur capture is proportional to from one-third power to the square root of the sulfur content (5), (6), (7). The differences in proportional coefficients may be explained due to differences in other test conditions.

Effect of Firing Rate on SO_2 Removal Rate. Fig. 5-2 shows the relation of the SO_2 removal rate to the firing rate in the furnace with the HS coal and the LS coal. The SO_2 removal rate increases as the firing rate decreases when the firing rate is in the range from 120 to 100 percent and decreases as the firing rate decreases when it is in the range from 100 to 80 percent. And, the SO_2 removal rate increases about three percent with the increment of over fire air from 20 to 25 percent, as shown in Fig. 5-2.

It is considered that the increment of the SO_2 removal rate with the decrement of the firing rate in the range from 120 to 100 percent is due to the increment of the residence time, which means the reaction time with lime and SO_2 gas, in the reaction zone. Moreover, it is considered that the decrement of the SO_2 removal rate with the decrement of the firing rate in the range from 100 to 80 percent is due to the decrement of the gas temperature in the limestone injection zone.

Effect of Over Fire Air on SO_2 Removal Rate. Fig. 5-3 shows the relation of the SO_2 removal rate to the amount of over fire air flow with the HS coal and the LS coal. The SO_2 removal rate increases with the increment of the over fire air flow.

In this test, the limestone was injected into the furnace after being mixed with the over fire air. It is considered that the increment of the SO_2 removal rate to a higher percent of OFA is based on a higher concentration of oxygen in the reaction zone of lime and SO_2. Changes in sorbent dispersion and mixing may also have an effect.

SO_2 Distribution and Sulfur Material Balance

Fig. 6-1 to Fig. 6-2 show the SO_2 concentration distribution along the flame axis with the two types of injecting methods. Here, the measuring points are shown in Fig. 3-2 as mentioned before.

Fig. 6-1 shows the result with the coal/limestone mixing system of the type (a). In this case, the limestone is injected into the furnace from the burner front. The SO_2 concentration gradually decreases from the burner front to the point 17 to 18 meters away from the burner front along the flame axis.

Fig. 6-2 shows the result with limestone injection through the OFA nozzle of type (c). In this case, the limestone is injected into the furnace from the OFA nozzles which are provided at the furnace side wall and located about 13 meters away from the burner front along the flame axis. As shown in Fig. 6-2, the SO_2 concentration abruptly decreases near the limestone injection port along the flame axis.

Fig. 6-3 shows a typical result from the sulfur mass ballances which were performed during the test program as a check on SO_2 measurements. In this figure, the inlet SO_2 means the SO_2 concentration calculated from the sulfur content in coal as shown in Table 1. The sulfur content in the coal showed slightly scattered values from day to day. It is felt that the error in sulfur material balance can be attributed to this and to unavoidable errors in sampling of ash. Nevertheless, a reasonably good sulfur balance was achieved.

Since the SO_2 removal rate is based on gaseous sulfur, which means SO_2 gas content in flue gas with and without limestone injection, it is considered that the SO_2 removal rates mentioned before have a considerably high degree of precision.

Flame Temperature and Burner Flame Condition

The flame temperature distribution measured by optical pyrometer in the direction of the flame axis comparing the firing rates with the HS coal and the LS coal are shown in Fig. 7-1.

From this figure, the flame temperature at the OFA port is from 1000 to 1100 degrees centigrade.

Burner flame conditions with the type (c) of injecting method is shown in Fig. 7-2. This figure shows the ignition condition and the flame pattern of the HS coal with the limestone injection using the pulverized-coal-fired low-NOx PM burner.

From this photograph it is obvious that the pulverized-coal-fired low-NOx PM burner is able to keep not only a low NOx level but also stable ignition and good combustion in the volatile matter combustion zone.

NOx Emission Characteristics

The relation of NOx emission to Ex.O_2 (oxygen concentration in flue gas) comparing the cases with and without limestone injection for HS coal and the LS coal are shown in Fig. 8-1 to Fig. 8-2 respectively.

NOx values with the injection of 20% OFA at four percent of oxygen concentration are around 110 ppm as shown in Fig. 8-1 and Fig. 8-2. Moreover, NOx value decreases about four ppm by the injection of the limestone. And, as shown in Fig. 8-1 to Fig. 8-2, the unburned carbon in fly ash is very low and slightly increases with the decrement of Ex.O_2.

INTERPRETATION OF TEST RESULTS AND DISCUSSION

When predicting the SO_2 removal rate in an actual boiler with the limestone injection system, it is required to understand the following items which were clarified in the series of the combustion tests.

- The optimum limestone injecting method is the injection through the over fire air nozzle system after mixing of the limestone with over fire air.

- The SO_2 removal rate increases with the increment of the over fire air flow mixed with the limestone and the NOx value decreases at the same time.

- There are three important parameters affecting SO_2 removal rate: the gas temperature, the residence time and the oxygen concentration in the reaction zone.
  The SO_2 removal rate increases with the increment of oxygen content in flue gas, and with the increment of the residence time. The latter may be interpreted as meaning a reduction of combustion rate in the furnace.

- The SO_2 removal rate increases with the increment of the sulfur content in coal.

As mentioned before, the SO_2 removal rate is greatly affected by the gas temperatures and the residence time in the reaction zone of SO_2 with limestone.

For the reasons mentioned above, it is most important to evaluate the relation between the gas temperature (or the flame temperature) and the residence time in the test furnace and/or an actual boiler for predicting the SO_2 reduction by the furnace limestone injection.

Fig. 9-1 shows the relation between the gas temperatures and the residence time at a full load of the actual pulverized-coal-fired boiler which was designed for bituminous coal. Here, the gas temperatures show the design values, calculated from the heat balance of the boiler.

And also, Fig. 9-2 shows the relation between the gas temperatures and the residence time at the 120 percent load with the PM burner used in the 4 ton/hour pulverized-coal fired test furnace. Here, the gas temperatures were measured by optical pyrometer for the combustion zone and by thermo-couple for the rear path zone.

Since Fig. 9-1 and Fig. 9-2 show good coincidences of the relations of gas temperatures and the residence time in the test furnace and the actual boiler, it would be considered that the SO_2 removal rate at full load of the actual pulverized coal fired boiler designed for bituminous coal coincides with the SO_2 removal rate at 120 percent load in the test furnace which is shown in Fig. 5-2.

Moreover, if the combustion rate and/or the heat release rate is lower as in the lignite fired boiler, the SO_2 removal rate is higher than that with the typical steaming-coal fired boiler.

Although no consideration is given to the mixing performance of limestone with flue gases, this is a very important factor in predicting the SO_2 removal rate in an actual pulverized-coal fired boiler.

A special consideration should be given to the mixing of limestone with the flue gas in an actual boiler furnace.

CONCLUSIONS

In a series of furnace limestone injection tests conducted at the MHI's 4 ton/hour test furnace with the pulverized-coal fired low-NO_x PM burner, it has been shown that 30 to 40 percent reduction of SO_2 at the Ca/S molar ratio of 2:1 is possible while maintaining low-NO_x combustion conditions. The optimum limestone injection location was through the overfire air ports located away from the main combustion zone. These results suggest that the limestone injection process can be decoupled from burner design and operation. Nevertheless, it appears that furnace limestone injection and low-NO_x combustion are compatible with each other for providing simultaneous NO_x and SO_2 removal.

These results can be used along with considerations of the design and operating conditions of the actual boiler in predicting the performance of limestone injection at full-scale.

The writers would feel greatly rewarded for their efforts if this paper should present a clue to the pollution control of pulverized-coal fired boilers.

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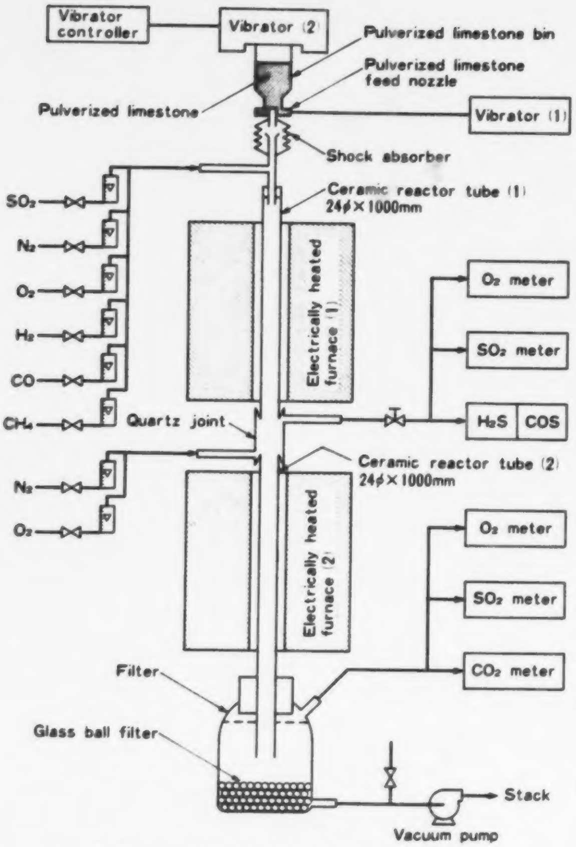


Vibrator controller
Vibrator (2)
Pulverized limestone bin
Pulverized limestone feed nozzle
Pulverized limestone
Vibrator (1)
Shock absorber
Ceramic reactor tube (1) 24φ×1000mm
SO₂
N₂
O₂
H₂
CO
CH₄
Electrically heated furnace (1)
O₂ meter
SO₂ meter
H₂S
COS
Quartz joint
Ceramic reactor tube (2) 24φ×1000mm
N₂
O₂
Electrically heated furnace (2)
O₂ meter
SO₂ meter
CO₂ meter
Filter
Glass ball filter
Stack
Vacuum pump

Fig. 1 Reactor tube test facility for SO_2 removal by pulverized limestone

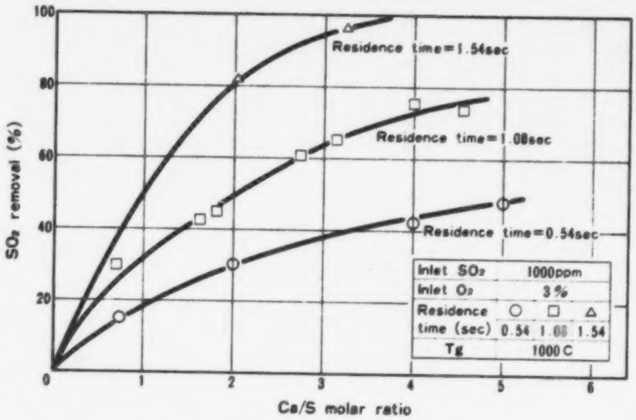


Fig. 2-1 Relation between SO_2 removal and Ca/S molar ratio (Gas temperature in primary reactor=1000°C)

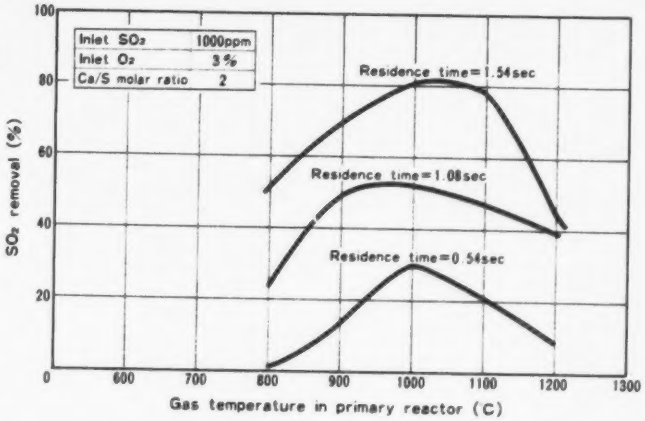


Fig. 2-2 Relation between SO_2 removal and gas temperature (Ca/S molar ratio=2)

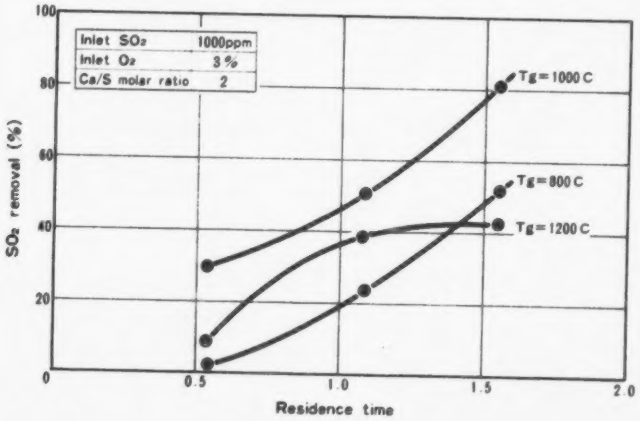


Fig. 2-3 Relation between SO_2 removal and residence time (Ca/S molar ratio=2)

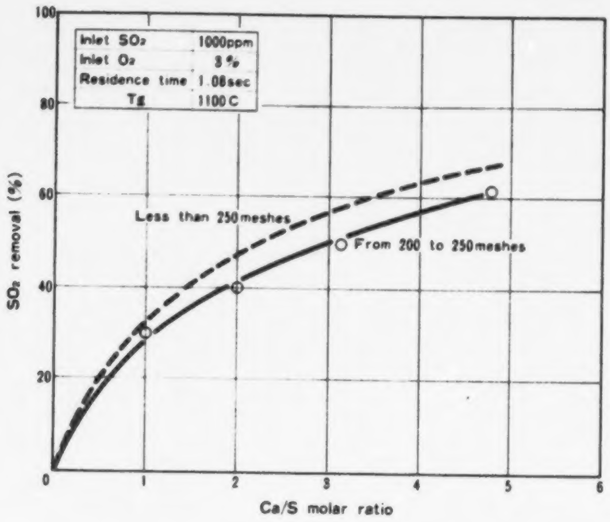


Fig. 2-4 Effect on fineness of limestone with SO_2 removal

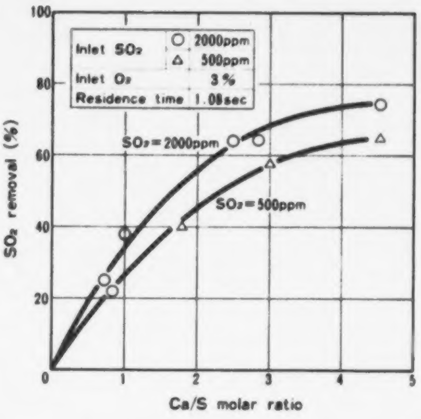


Fig. 2-5 Relation between SO_2 removal and Ca/S molar ratio with different SO_2 concentration

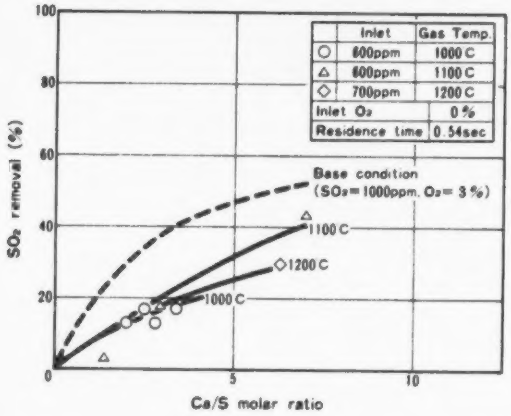


Fig. 2-6 Relation between SO_2 removal and Ca/S molar ratio with 0% O_2 atmosphere

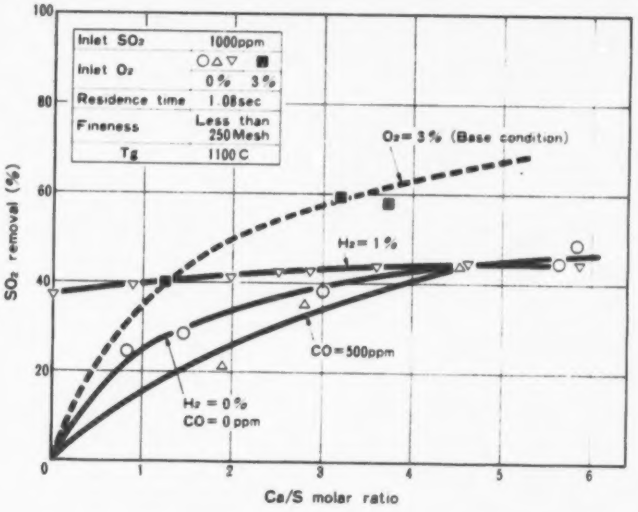


Fig. 2-7 Effect on inlet gas composition with SO_2 removal

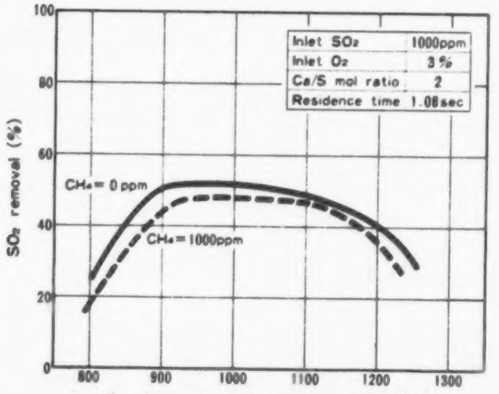


Fig. 2-8 Relation between SO_2 removal and gas temperature (Residence time=1.08sec)

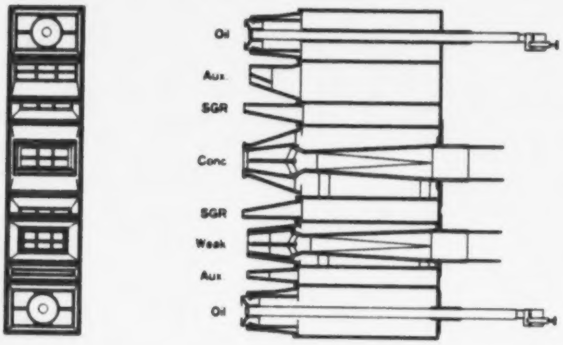

Oil
Aux.
SGR
Conc
SGR
Weak
Aux
Oil

Fig. 3-1 Configuration of pulverized coal-fired low-NOx PM burner

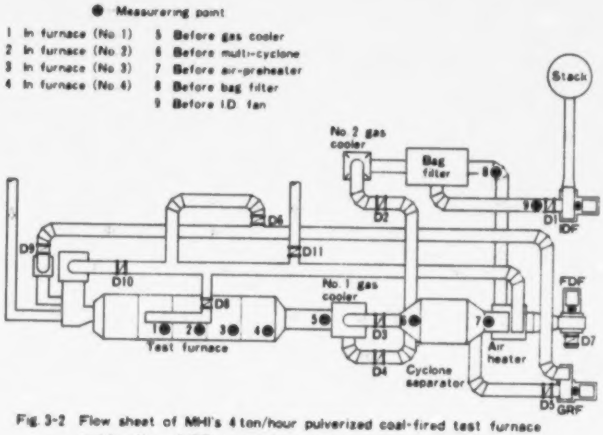
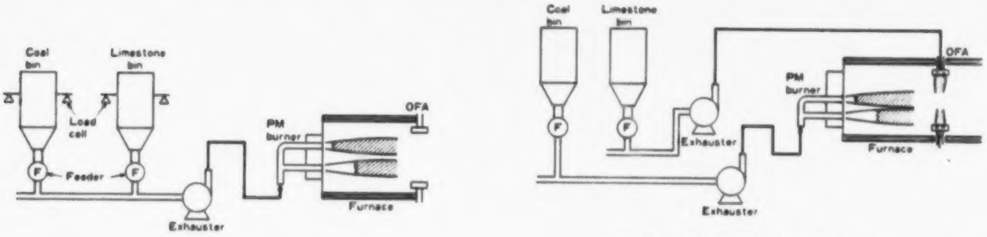
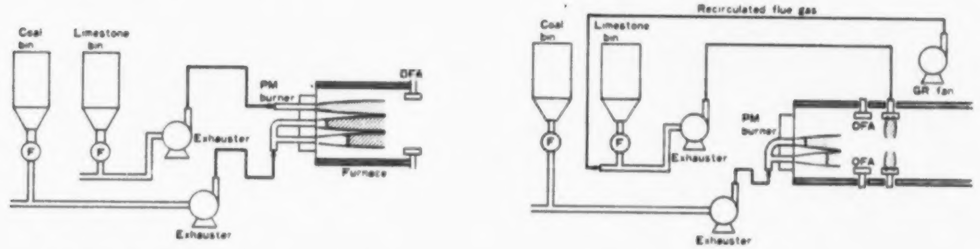

● Measurering point
1 In furnace (No 1)
2 In furnace (No 2)
3 In furnace (No 3)
4 In furnace (No 4)
5 Before gas cooler
6 Before multi-cyclone
7 Before air-preheater
8 Before bag filter
9 Before I.D. fan
Stack
No 2 gas cooler
Bag filter
D1
IDF
D2
D6
D9
D11
D10
D8
No. 1 gas cooler
FDF
Test furnace
D3
D4
Cyclone separator
Air heater
D7
D5
GRF

Fig. 3-2 Flow sheet of MHI's 4 ton/hour pulverized coal-fired test furnace and location of SO_2 measuring point


Coal bin
Limestone bin
Load cell
Feeder
F
Exhauster
PM burner
OFA
Furnace
Coal bin
Limestone bin
F
Exhauster
PM burner
OFA
Furnace
Exhauster

Type (a) : Coal/limestone mixing system

Type (c) : System through the OFA nozzle


Coal bin
Limestone bin
F
Exhauster
PM burner
OFA
Furnace
Exhauster
Recirculated flue gas
Coal bin
Limestone bin
GR fan
F
Exhauster
PM burner
OFA
OFA
Exhauster

Type (b) : System through the auxiliary air nozzle

Type (d) : System through the GR nozzle

Fig. 3-3 Injecting system of the coal and the limestone

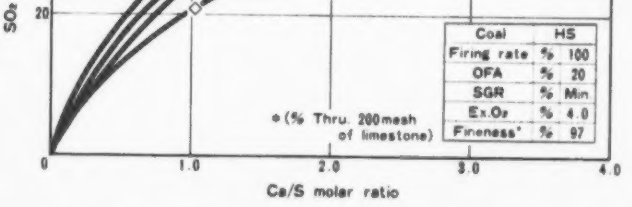
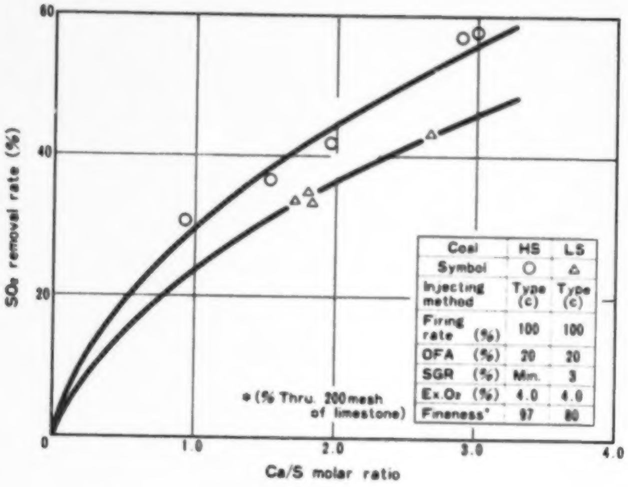
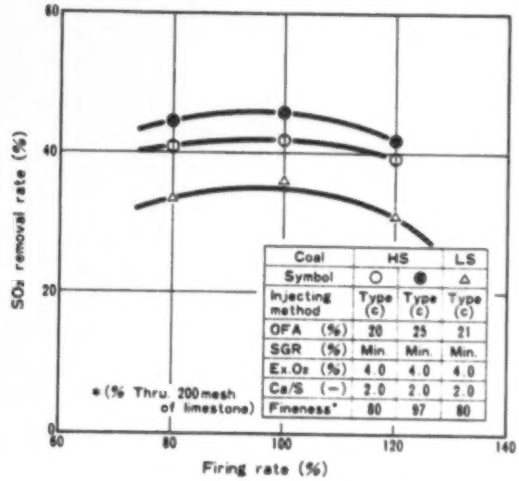


Fig. 4-1 Comparison of SO_2 removal rates with types of injecting methods



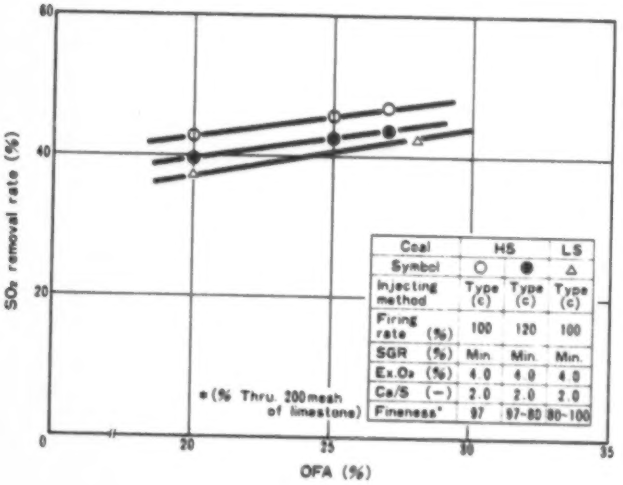
Coal	HS	LS
Symbol	○	△
Injecting method	Type (c)	Type (c)
Firing rate (%)	100	100
OFA (%)	20	20
SGR (%)	Min.	3
Ex.O₂ (%)	4.0	4.0
Fineness*	97	80

Fig. 5-1 Effect of Ca/S molar ratio on SO₂ removal rate



Coal	HS		LS
Symbol	○	●	△
Injecting method	Type (c)	Type (c)	Type (c)
OFA (%)	20	25	21
SGR (%)	Min.	Min.	Min.
Ex.O₂ (%)	4.0	4.0	4.0
Ca/S (−)	2.0	2.0	2.0
Fineness*	80	97	80

Fig. 5-2 Effect of firing rate on SO₂ removal rate



Coal	HS		LS
Symbol	○	●	△
Injecting method	Type (c)	Type (c)	Type (c)
Firing rate (%)	100	120	100
SGR (%)	Min.	Min.	Min.
Ex.O₂ (%)	4.0	4.0	4.0
Ca/S (−)	2.0	2.0	2.0
Fineness*	97	97~80	80~100

Fig. 5-3 Effect of OFA on SO₂ removal rate

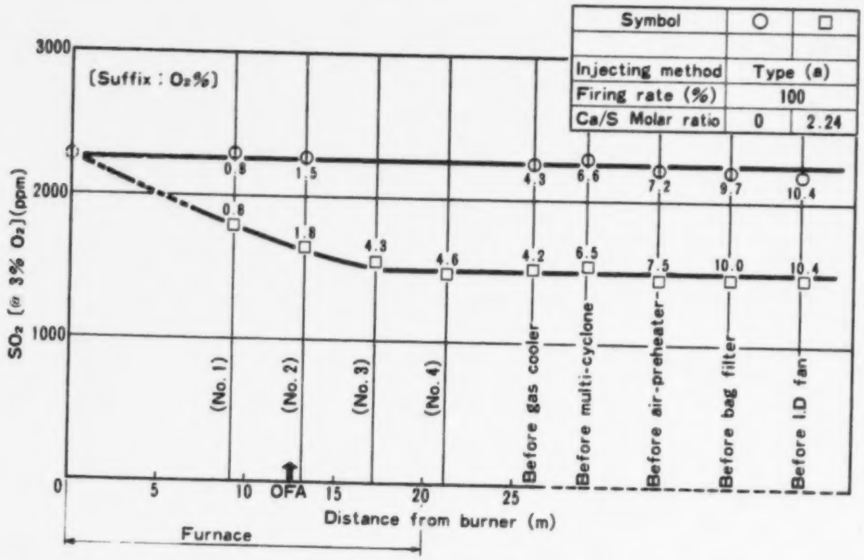


Fig. 6-1 SO_2 distribution along the flame axis (Type (a))

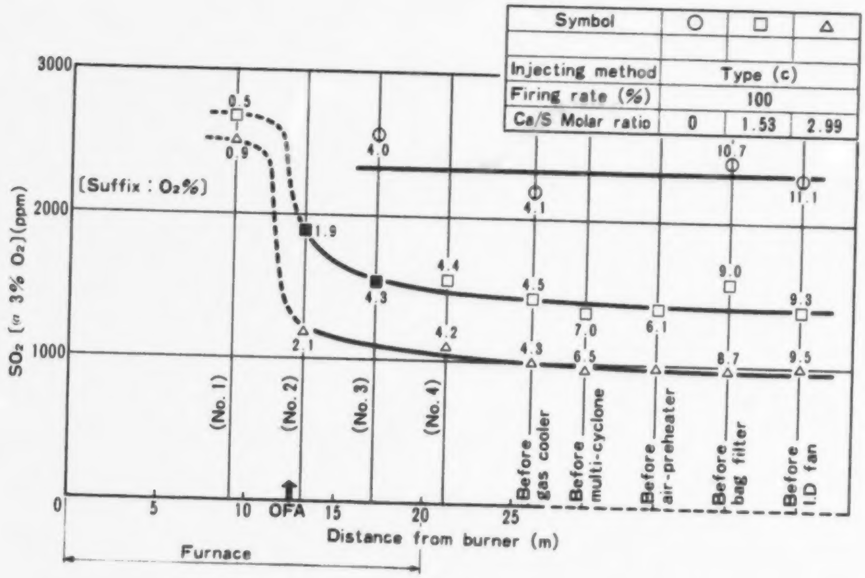


Fig. 6-2 SO_2 distribution along the flame axis (Type (c))

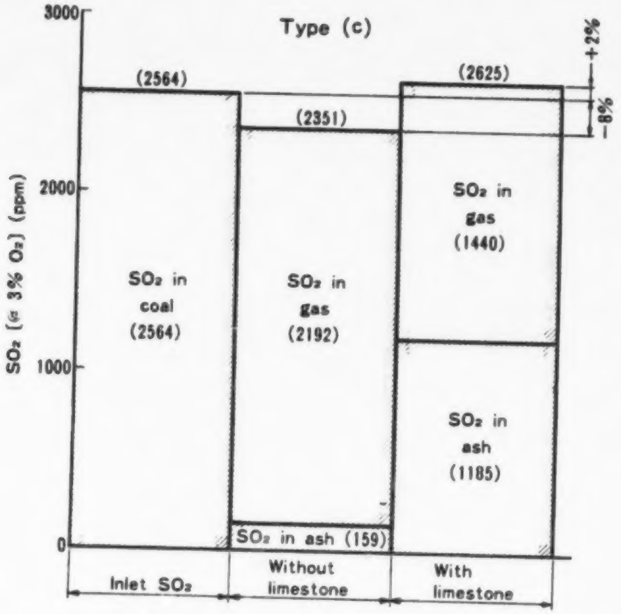
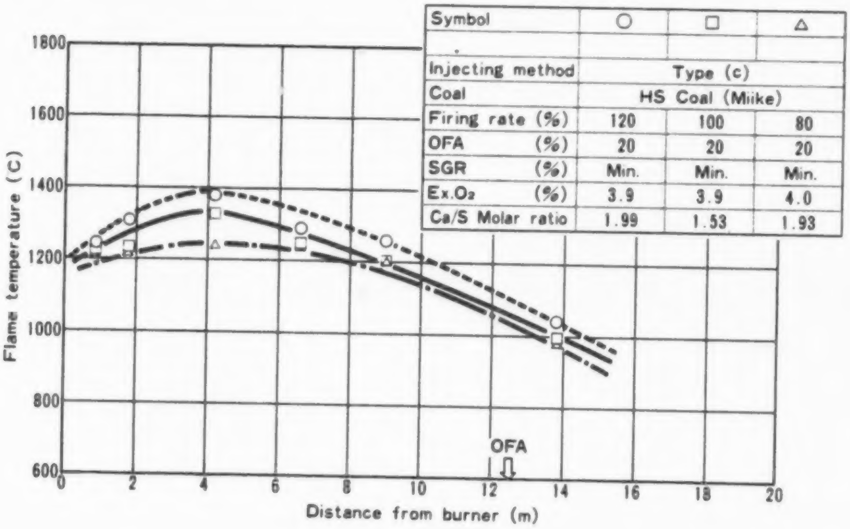
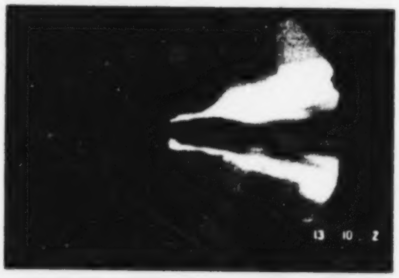


Fig. 6-3 Mass balance of sulfur with HS coal at furnace outlet



Symbol	○	□	△
Injecting method	Type (c)		
Coal	HS Coal (Miike)		
Firing rate (%)	120	100	80
OFA (%)	20	20	20
SGR (%)	Min.	Min.	Min.
Ex.O₂ (%)	3.9	3.9	4.0
Ca/S Molar ratio	1.99	1.53	1.93

Fig. 7-1 Flame temperature distribution along the flame axis with different firing rates



Front view of the flame around the burner front

Fig. 7-2 Combustion flame with injecting method in the system through the OFA nozzle (Type (c))

Symbol		○ ●	□ ■	△ ▲
Coal	—	HS Coal (Miike)		
Firing rate	%	120	120	100
OFA	%	20	20	20
SGR	%	Min.	Min.	Min.
Ex.O₂	%	—	—	—
Ca/S Molar ratio	—	0	≅2	0

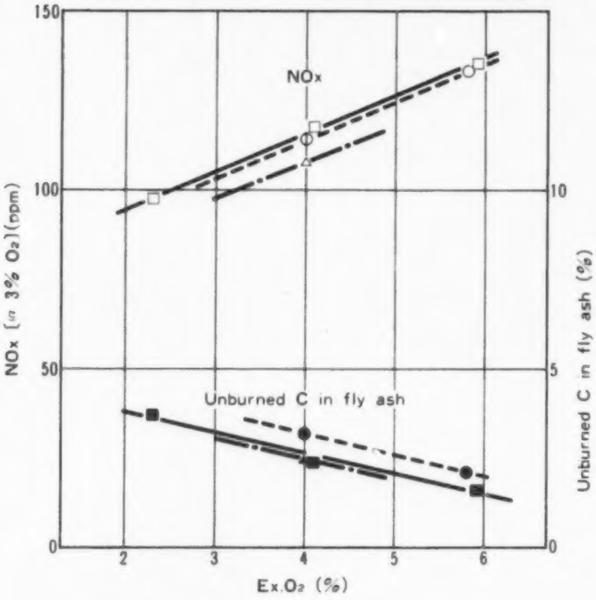


Fig. 8-1 NOx and unburned C in fly ash vs. Ex.O₂ with HS coal (Limestone injecting method : Type (c))

Symbol		○ ●	□ ■	△ ▲
Coal	—	LS Coal (Plateau)		
Firing rate	%	100	100	120
OFA	%	20	20	20
SGR	%	Min.	Min.	Min.
Ex.O₂	%	—	—	—
Ca/S Molar ratio	—	0	≒2	0

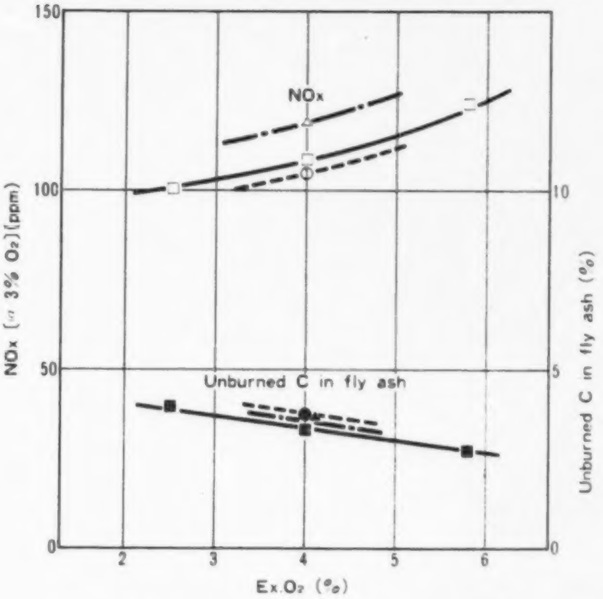


Fig. 8-2 NOx and unburned C in fly ash vs. Ex.O₂ with LS coal (Limestone injecting method : Type (c))

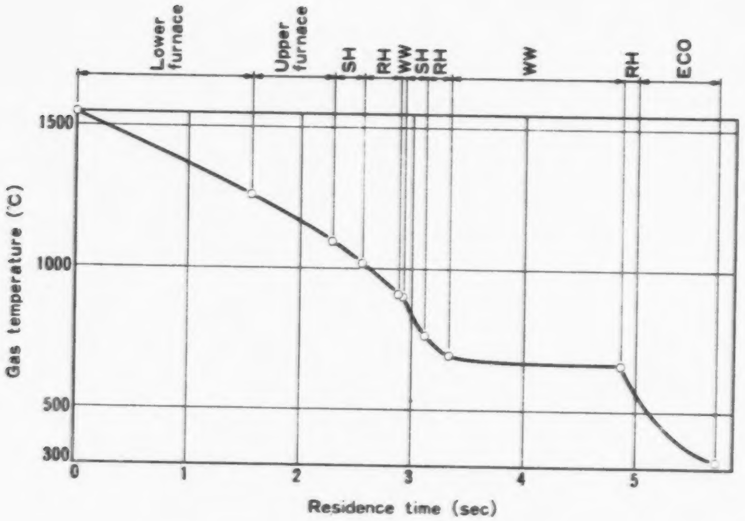


Fig. 9-1 Relation between gas temperature and residence time in actual boiler

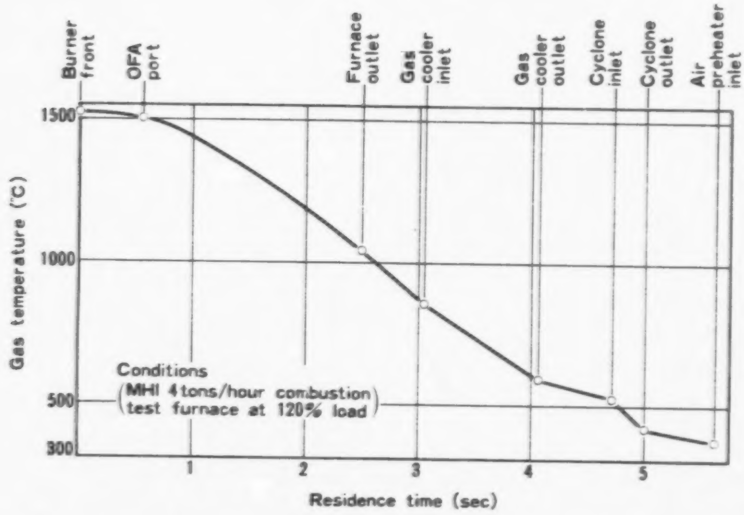


Fig. 9-2 Relation between gas temperature and residence time in MHI 4tons/hour combustion test furnace

Table 1 Analysis of coal used

Item		Unit	HS Coal (Hiike Coal)	LS Coal (Plateau Coal)
HHV (Dry)		kcal/kg	6.830	6.700
Surface moisture		%	0.8	3.1
Proximate analysis (Dry base)	Inherent moisture	%	1.1	4.1
	Fixed carbon	%	40.8	48.4
	Volatile matter	%	40.4	36.1
	Ash	%	17.7	11.4
	Total	%	100.0	100.0
	Total S	%	3.11	0.75
	Fuel ratio (F.C/V.M)	—	1.01	1.34
Ultimate analysis (Moisture free)	C	%	69.6	72.0
	H	%	5.5	5.1
	O	%	3.2	8.8
	N	%	0.98	1.56
	S (combustible)	%	2.85	0.64
	S (uncombustible)	%	0.30	0.14
Fusibility (DIN/ASTM)	Softening temp.	℃	1.260/1.235	1.265/1.280
	Fusion temp.	℃	1.320/1.245	1.380/1.330
	Fluid temp.	℃	1.365/1.260	1.495/1.340

Table 2 Analysis of limestone used

		Unit	Limestone
Constituent analysis	CaO	%	55.1
	MgO	%	0.4
	SiO_2	%	0.1
	$A\ell_2O_3$	%	0.1
	Fe_2O_3	%	—
	Ingition loss	%	44.3
Specific gravity		g/cm³	2.7

Table 3 Items, methods and locations of measurements

Item		Method	Location
Flue gas analysis	O_2	Zirconia cell	Flue gas duct
	CO_2	N.D.I.R. and drager detector	
	CO		
	NO_x	Chemiluminescent analyzer	
	SO_x	Ultra violet absorption analyzer and calorimetric analysis	
Flame temp.		Optical pyrometer	Observation ports at furnace
Heat flux		Thermo pile heat flow detector	〃

PERFORMANCE OF SORBENTS WITH AND WITHOUT ADDITIVES, INJECTED INTO A SMALL INNOVATIVE FURNACE

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ABSTRACT

The Environmental Protection Agency (EPA) Innovative Furnace was used to develop information on the performance of sulfur sorbents with and without additives. The sorbents were injected at two points in a furnace using a low-NO_x type burner fired at a 14 kW thermal input rate on coal or liquefied petroleum gas (LPG) propane. The sorbents, a calcitic limestone (Vicron), a pressure-hydrated dolomite, and pure calcium hydroxide [$Ca(OH)_2$], were tested at Ca/S ratios of 1 and 2. The additives, $NaHCO_3$ and Na_2CO_3, mixed with the sorbent, were tested at 5 weight percent of the sorbent. Sodium carbonate (Na_2CO_3) appears to be an effective additive, giving increases in sulfur reduction of 6 to 12 percentage points, depending upon the amount of additive, the sorbent, and injection location.

INTRODUCTION

For the limestone injection multistage burner (LIMB) program to achieve complete success, sulfur capture greater than that exhibited to date by limestone alone must be achieved. This project was undertaken to determine the effects of additives on the utilization or sulfur capture performance of several sorbents. The additives tested were those found most effective in bench-scale tests and with high potential for commercial use; i.e., not toxic and relatively low in cost. The sorbents used were chosen to represent sorbent types being considered; i.e., calcium carbonate (Vicron), calcium hydroxide, and hydrated dolomite (Genstar). Vicron performance has been well characterized by previous LIMB work. The coal used is one on which an extensive data base exists and which has been used by several investigators.

This is a status report on the first of a series of investigations.

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DISCUSSION OF PROJECT

EPA Innovative Furnace

The EPA innovative furnace is a modified copy of a furnace built by Energy and Environmental Research Corporation (EERC). The unit is a 6-in. (155-mm) internal diameter down-fired unit. Three burner configurations may be used: an axial-fired, a radial-fired, and a premix configuration with provision for tangential or swirl air. Each of the three configurations may employ the distributed-mixing burner concept. In the premixed burner, this is accomplished by mixing less than the total air in the burner and adding the remainder of the air after the burner.

The firing rate of the furnace is adjustable with a nominal rating of 100,000 Btu/hr (29.6 kW) or about 3.2 kg coal/hr. Stable operation at a rate of about 1.4 kg coal/hr (42,000 to 50,000 Btu/hr) is a normal mode for testing. The unit may be fired on either propane or coal. Normal practice is to fire the unit on propane, unattended, over weekends, Friday afternoon to Monday morning, and overnight, 5:30 p.m. to 8:00 a.m. This allows thermal stabilization of the unit and avoids shock to the refractory by maintaining the unit at the testing temperature.

The unit is of conventional construction with rolled steel rings 30 in. (762 mm) in diameter and 1 ft (300 mm), 1.5 ft (450 mm), or 2 ft (600 mm) high. The steel rings are insulated by four courses of refractory beginning on the outside with a good insulating, low strength castable block mix refractory, progressing inward with castable insulation, following with Castolite 30,* and ending on the inside with a high strength, erosion resistant "hard face" refractory such as Green Cast 97. After casting the refractory into the steel rings, the rings are "stacked" using a gasket made of Kaowool or similar material on the outer periphery. A small amount of uncured refractory is applied around the matching faces of the inner central passage to prevent gas migration to the outer steel shell. Both the gasket and the uncured inner seal material are formed and spread by the weight of the ring and the clamping force of the bolted ring flanges, thus ensuring a good seal at each joint. The joint surfaces of the combustion passage are "faired in" and troweled to give a reasonably smooth and uniform combustion passage.

Inspection or view ports are provided, one a 2-in. (52-mm) circular port at about 7-1/2 in. (190 mm) from the burner tip, and a rectangular port 6 in. x 4 in. (155 mm x 100 mm), centered 23 in. (585 mm) below the burner tip. Nine thermocouples, embedded in the refractory approximately 1/2-in. (12 mm) from the combustion gas central passage, are spaced over the 11-ft (30.48-cm) long furnace section. There are nine ports, approximately opposite the thermocouple locations, that are usable for either sampling or injection. Three larger rectangular ports are available for the insertion of chokes and cooling coils to "stage" the combustion or divide the furnace into two or three zones with varied stoichiometry; the first is usually a "fuel-rich" or "reducing" zone, and the last, an air-rich or burnout zone. The final furnace section contains cooling water coils to quench any reactions before the sample is extracted for the continuous monitors. See Figure 1 for diagram.

Solid fuel, such as coal, is metered from a K-Tron* loss-in-weight feeder. A similar feeder, but suited to delivery of a smaller amount, meters the sorbent, such as limestone or lime. The sorbent material is aspirated and transported by air and injected into the furnace through a water-cooled probe.

(*) Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. EPA.

Operating conditions and emissions are monitored using the following instruments:

Digistrip III™ Data Logger
Continuous Monitors:

CO	Beckman Model 864 Infrared
CO_2	Beckman Model 864 Infrared
O_2	Beckman Model 755
SO_2	Anacon Model 207 U.V.
NO, NO_2, NO_x	Thermoelectron Model 10AR
HC	Beckman Model 402

Thermocouples, both B&K types, embedded or sealed in the refractory.

In addition, gas temperatures are measured using suction pyrometry with stabilized run conditions equal to those in the tests. No significant temperature profile difference was found between gas firing and coal firing at equal heat input rates, based on fuel heating value and excess air conditions. The actual gas temperatures for different positions at the test conditions are thus established, and no conversion from the thermocouple temperature to the gas temperature is required. The relationship between thermocouple temperature, at a given point under known conditions, and the gas temperature is known from the previous suction pyrometry work. Periodically, suction pyrometry tests are performed during emission testing to confirm the gas temperatures found in earlier suction pyrometry testing.

The SO_2 readings and NO_x readings from the continuous monitors are compared with those from EPA Methods 6 and 7 (wet chemistry). It would appear from preliminary results that the SO_2 readings are within 10 percent of the values of EPA Method 6, but that the NO_x readings are more than 10 percent from the values of EPA Method 7. This is being investigated further. Some difficulty (leaking glass-to-glass seal on the impinger vials) was encountered in collecting Method 7 samples.

There is a provision to inject pure SO_2 into the propane immediately before the burner to give a sulfur input equal to that when coal is fired. The SO_2 is metered into the fuel gas through a rotameter, and the SO_2 measured in the stack is compared to the level computed from fuel analysis and measured input of the fuel and air.

Material Description

The LPG propane used is supplied by FCX, a farmers cooperative. Past experience indicated that some variance in composition from one tank fill to the other was possible. This variance, if present, did not manifest itself as changes in the furnace conditions.

The Vicron limestone is a material designated as 45-3, in reference to the nominal particle size range of the cut or fraction used. When tested, 99.2 percent passed through a 60-mesh sieve. This material has been used and reported in a number of sorbent tests by Energy and Environmental Research Corporation, Acurex Corporation, and Southern Research Institute. This particular batch was obtained from Acurex Corporation in 1982.

The material referred to as "Genstar Henderson" is $MgO \cdot CaO$ pressure-hydrated to $Mg(OH)_2 \cdot Ca(OH)_2$ from the Henderson, Nevada, Plant of the Genstar Corporation. It is a commercial product. Sieve testing gave 97.1 percent passing through a 30-mesh screen and 66.3 percent passing through a 60-mesh screen.

The calcium hydroxide is a technical grade laboratory supply item, Fisher number C-88. No special storage precautions, other than closing the bag after removing the test charge, were used. The sieve test showed 99.5 percent passing through a 60-mesh sieve.

The sodium bicarbonate used is a laboratory reagent grade, Fisher number S-233. In a sieve test, 99.7 percent passed through a 60-mesh sieve.

The sodium carbonate used is a laboratory reagent grade, Fisher number S-263. In a sieve test, 100 percent passed through a 30-mesh sieve and 26.3 percent passed through a 60-mesh sieve.

The coal used, a Pittsburgh number 8 seam coal, was obtained from Acurex Corporation in July 1983. The Commercial Testing and Engineering (CTE) analysis furnished with the coal was confirmed by an analysis performed by Pennsylvania Electric Company (PENELEC) in November 1983. PENELEC analyzed three composite samples submitted from the coal shipped to EPA, Research Triangle Park, NC, from Acurex Corporation. The coal is stored in 50-lb (22.7 kg) bags in an unheated, enclosed storage building. Table 1 presents a summary of coal analyses on an as-received basis.

PROCEDURES

A standardized test plan for the evaluation of sorbents and sorbent/additive mixtures was followed. The plan called for holding the furnace firing conditions constant while varying the sorbent feed rate, sorbent injection point, and the fuel/sulfur type (propane or C_3H_8/SO_2, Pittsburgh number 8 coal). A test matrix was devised such that the three sorbents, with and without each of the two additives, would be evaluated under similar conditions according to the standardized test plan. Figure 2 illustrates the test matrix used in this study.

Pretest Preparations

Before testing a new sorbent, procedures to ensure correct feeding were performed. The feed rates required to obtain Ca/S ratios of 1 and 2 in the combustion zone were calculated from the chemical analysis of the sorbent. The sorbent feeder was recalibrated for each sorbent of different bulk density. If the new sorbent material contained an additive, the sorbent and additive were thoroughly mixed in the turbo-tumbler for 30 minutes.

Routine Testing

Throughout the study, the furnace firing conditions were held constant. The firing rate was 47,300 Btu/hr (14 kW), the air stoichiometric ratio (S.R.) was 1.25, and the combustion air was preheated to 250°F (121°C).

The testing of a sorbent or sorbent/additive mixture was divided into two 1-day test periods. On one day, the sorbent material was injected with the fuel through the burner. On the other day, the sorbent material was injected through a water-cooled probe 32 in. (0.8 m) below the burner. The testing routine given below was followed at each sorbent injection point.

1. Switch from propane (C_3H_8) to Pittsburgh number 8 fuel, and adjust air supplies to maintain an air S.R. = 1.25.

2. Insert the sorbent injection probe (if necessary).
3. Calibrate the continuous emission monitors.
4. Ensure stable baseline combustion conditions.
5. Perform a minimum of two sorbent injections at a Ca/S ratio = 1, gathering [SO_2] reduction data.
6. Perform a minimum of two sorbent injections at a Ca/S ratio = 2, gathering [SO_2] reduction data.
7. Switch from Pittsburgh number 8 coal to C_3H_8 fuel, and adjust air supplies to maintain an S.R. = 1.25.
8. Ensure proper combustion conditions (without SO_2 doping).
9. Meter SO_2 into the C_3H_8 fuel to provide sulfur loading equivalent to the sulfur content of Pittsburgh number 8 coal.
10. Allow SO_2 concentration in flue gas to stabilize.
11. Perform a minimum of two sorbent injections at a Ca/S ratio = 1, gathering [SO_2] reduction data.
12. Perform a minimum of two sorbent injections at a Ca/S ratio = 2, gathering [SO_2] reduction data.
13. Check the zero and span of the continuous monitors.
14. Shut off SO_2 supply; purge lines.
15. Remove sorbent injection prcbe (if necessary).
16. Reset combustion air supplies for overnight operation.

Data Collection and Reduction

A Digistrip III data logger was used to collect experimental data from the continuous emission monitors and the thermocouples. The data logger was programmed to report instantaneous and 2-minute averages of flue gas concentrations. In addition to the data logger, strip chart recorders were used as a visual aid to the operator to ensure stable furnace conditions.

The baseline [SO_2] was taken as a 2-minute average when the strip chart recorder indicated relatively stable conditions. The sorbent feeder was started exactly on the data gathering interval. The reduced [SO_2] was taken as the first stable 2-minute average after the initiation of sorbent injection. The sorbent injection intervals were as brief as possible to avoid possible effects from sorbent buildup on the furnace wall. To ensure the elimination of a possible bias due to wall effects, the [SO_2] was required to return to baseline conditions within 10 minutes of the cessation of sorbent feeding for the data to be considered valid. The average response time of the SO_2 analyzer is about 2 minutes.

In order to correct for slight variations in furnace conditions, all $[SO_2]$'s were corrected to zero percent O_2 conditions by Eq. (1).

$$[SO_2]_{0\%\ O_2} = [SO_2]_{obs} \frac{21}{21 - [O_2]_{obs}} \tag{1}$$

The corrected $[SO_2]$'s and the Ca/S (mol/mol) ratio are then used to determine the percent Ca utilization by Eq. (2).

$$\%\ \text{Ca utilization} = \left(\frac{\dfrac{[SO_2]_{\text{baseline, }0\%\ O_2} - [SO_2]_{\text{reduced, }0\%\ O_2}}{[SO_2]_{\text{baseline, }0\%\ O_2}}}{(Ca/S)} \right) \tag{2}$$

Figure 3 is a reproduction of a typical strip chart trace of $[SO_2]$ through two sorbent injections. The figure is only for illustrative purposes since experimental data is gathered digitally by the data logger; however, the trace provides a guide to the eye and an indication of equipment performance.

In this case the sorbent utilization is approximately 15 percent since the $\Delta\ [SO_2]$ is approximately 30 percent and the Ca/S ratio is 2.

Results

Figure 4 illustrates the average performance of each of the three sorbents with no additives at two injection locations while burning coal. Figure 5 shows the relative performance of Vicron injected 32 in. (0.8 m) below the burner while firing with C_3H_8 and coal with and without additives. Figure 6 shows the relative performance of Genstar-Henderson injected 32 in. (0.8 m) below the burner while firing with C_3H_8 and coal with and without additives. Figure 7 shows the relative performance of calcium hydroxide injected 32 in. (0.8 m) below the burner while firing with C_3H_8 and coal with and without additives.

Each bar of the figures represents a minimum of four data points: two utilizations determined at a Ca/S of 1, and two at Ca/S of 2. Most bars represent six or eight data points. The utilizations computed in Eqs. (1) and (2) are averaged for the graphs. Results of sorbent/additive mixture injection through the burner are not presented because they are still under study.

Discussion of Data

Figure 4 shows the performance of the three sorbents, with no additives, at two injection locations while burning coal. When injected through the burner, the Vicron was only 2 percentage points below the performance when injected 32 in. (0.8 m) below the burner at a more favorable temperature window. The lower injection point put the material in at a gas temperature of about 2200 to 2300°F (1204 to 1260°C).

The hydroxide and di-hydrate showed a greater increase in utilization percentage when moved to the downsteam injection location.

The Vicron material, shown in Figure 5, exhibited little change from gas to coal firing when no additive was used. The effect of the carbonate additive with the Vicron was very pronounced in gas firing, increasing the utilization from 15 percent to over 28 percent. The effect of the carbonate additive was much less when used with coal firing. It gave only an increase from just under 14 percent to just under 21 percent in the coal-fired case. The bicarbonate showed some reduction in effectiveness going from gas to coal firing.

From the above, one could say that, whatever the capture process is for Vicron alone, it is not significantly sensitive to coal ash interactions. However, when an effective additive such as the sodium carbonate is used, the capture process becomes more sensitive to coal/ash interaction.

With the above in mind, one turns to the Genstar, Figure 6. This material is a pressure-hydrated di-hydrate of the approximate formula $Ca(OH)_2 \cdot Mg(OH)_2$. Here the pattern is reversed. That is, the Genstar shows better utilization under coal-firing conditions than under gas-firing conditions, both with and without the additives, sodium carbonate and sodium bicarbonate. Unlike the previous case, here the bicarbonate is the more effective additive.

One could make the conjecture that coal/ash interactions help the sulfur capture process in a di-hydrate addition and that less improvement (in percentage points of utilization) is possible through the use of additives with a di-hydrate compared to the improvement possible with a limestone.

Figure 7 shows that a pure (technical grade) calcium hydroxide shows little change from gas to coal firing in the percentage utilization either with or without additives. Sodium carbonate is the more effective additive giving about 10 percentage points improvement under coal-fired conditions versus only about 3 percentage points for the bicarbonate. From the above, one can say that the sulfur capture process for the hydroxide case is not greatly affected by the coal/ash interactions, either with or without additives.

CONCLUSIONS

For Vicron limestone, calcium hydroxide, or dolomite di-hydrate, the better injection point is below or past the burner rather than through the burner for coal firing.

The sodium additives, sodium bicarbonate and sodium carbonate, provide an enhancement of calcium utilization and sulfur capture when used at a level of 5 weight percent of the sorbent with any of the calcium sorbents named above.

The di-hydrate material (Genstar Henderson) gave better utilization with coal firing than gas firing, both with and without additives.

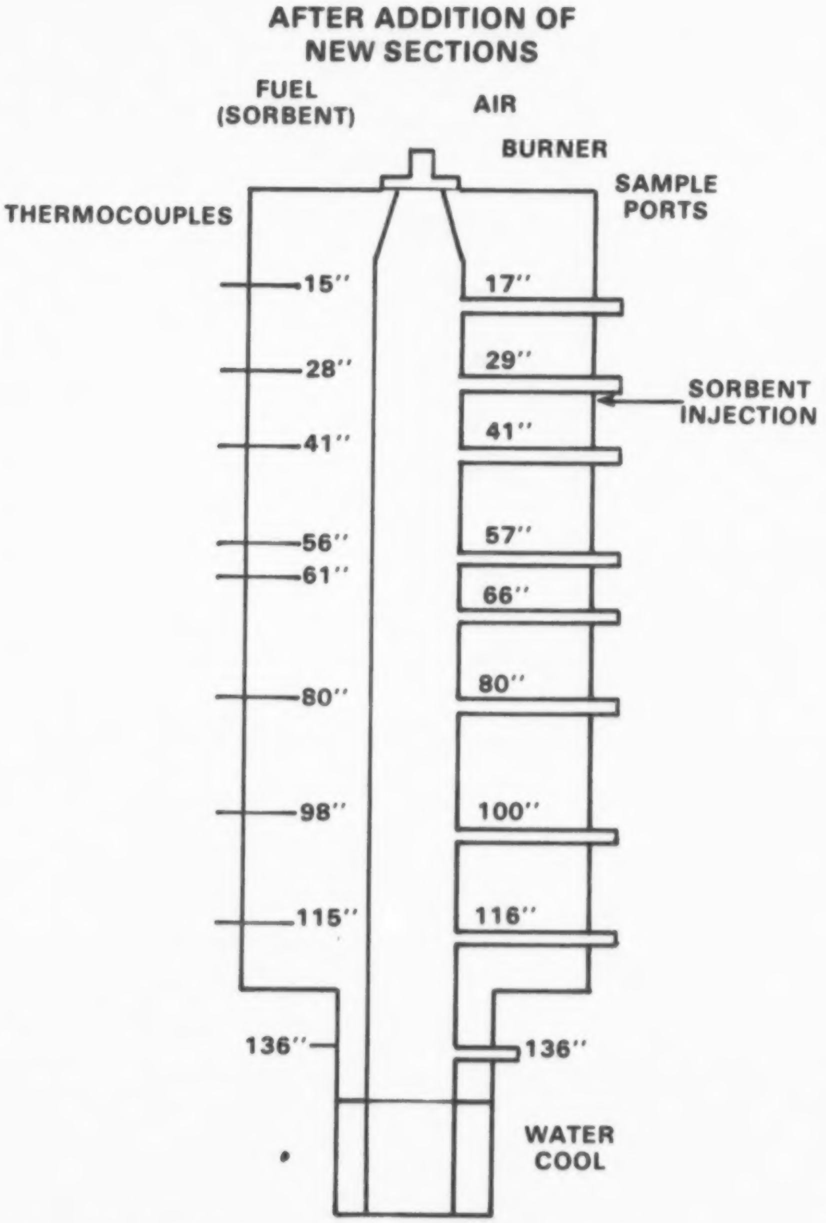
AFTER ADDITION OF NEW SECTIONS
FUEL (SORBENT)
AIR
BURNER
SAMPLE PORTS
THERMOCOUPLES
15"
28"
41"
56"
61"
80"
98"
115"
136"
17"
29"
41"
57"
66"
80"
100"
116"
136"
SORBENT INJECTION
WATER COOL

Figure 1. Diagram of LIMB furnace showing locations of Type B thermocouples, sampling ports, and sorbent injections.

		Vicron-45			Genstar-Henderson			Calcium Hydroxide		
		No Additive	5% $NaHCO_3$	5% Na_2CO_3	No Additive	5% $NaHCO_3$	5% Na_2CO_3	No Additive	5% $NaHCO_3$	5% Na_2CO_3
Coal	Inject at Burner									
	Inject Below Burner									
C_3H_8	Inject at Burner									
	Inject Below Burner									

Figure 2. Experimental test matrix.

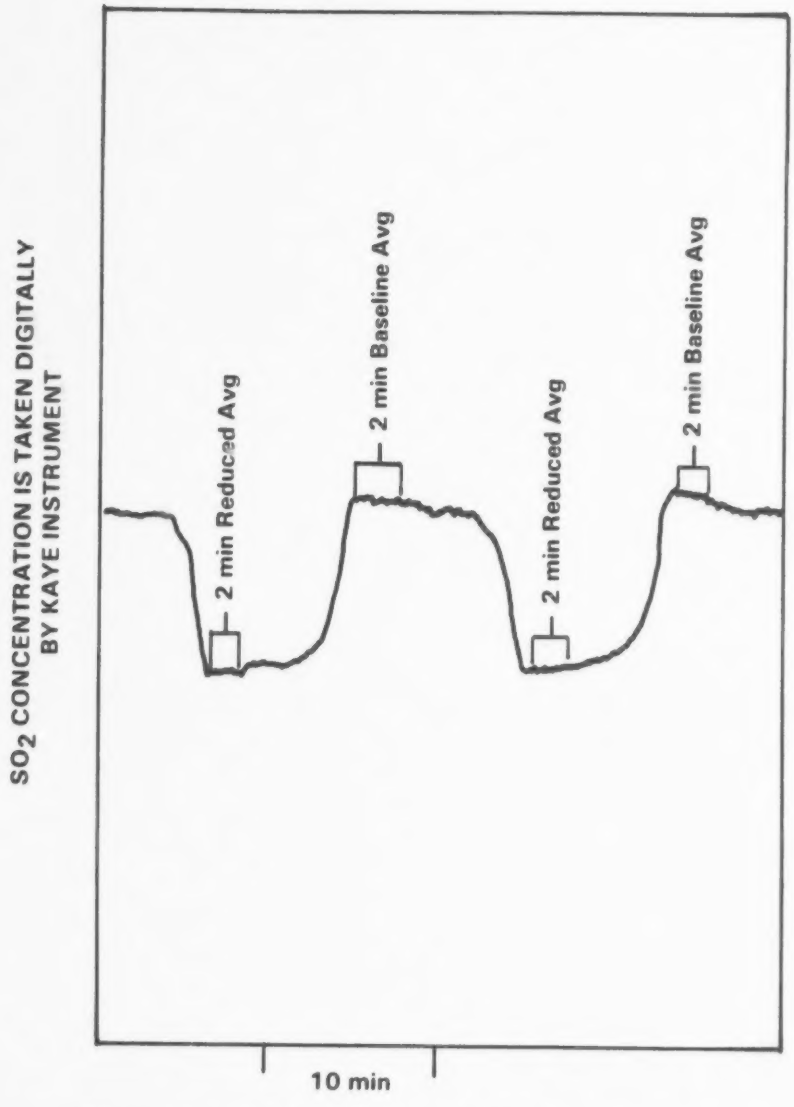

Figure 3. Typical [SO_2] strip chart trace during two sorbent injections.

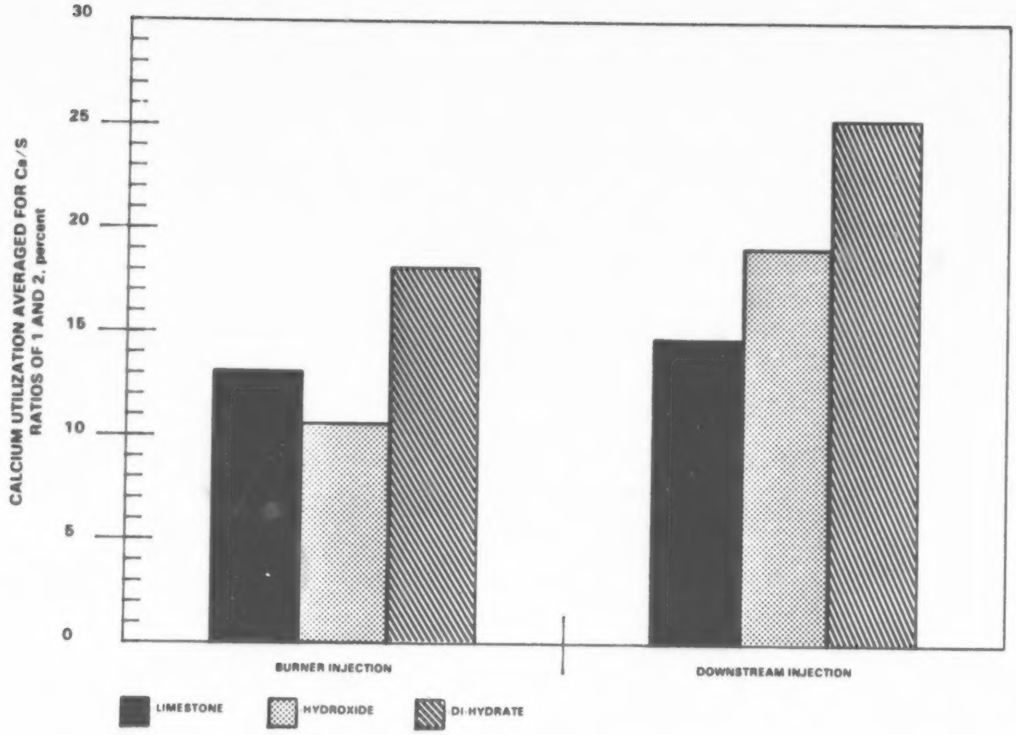

Figure 4. Performance of sorbents at two injection points.

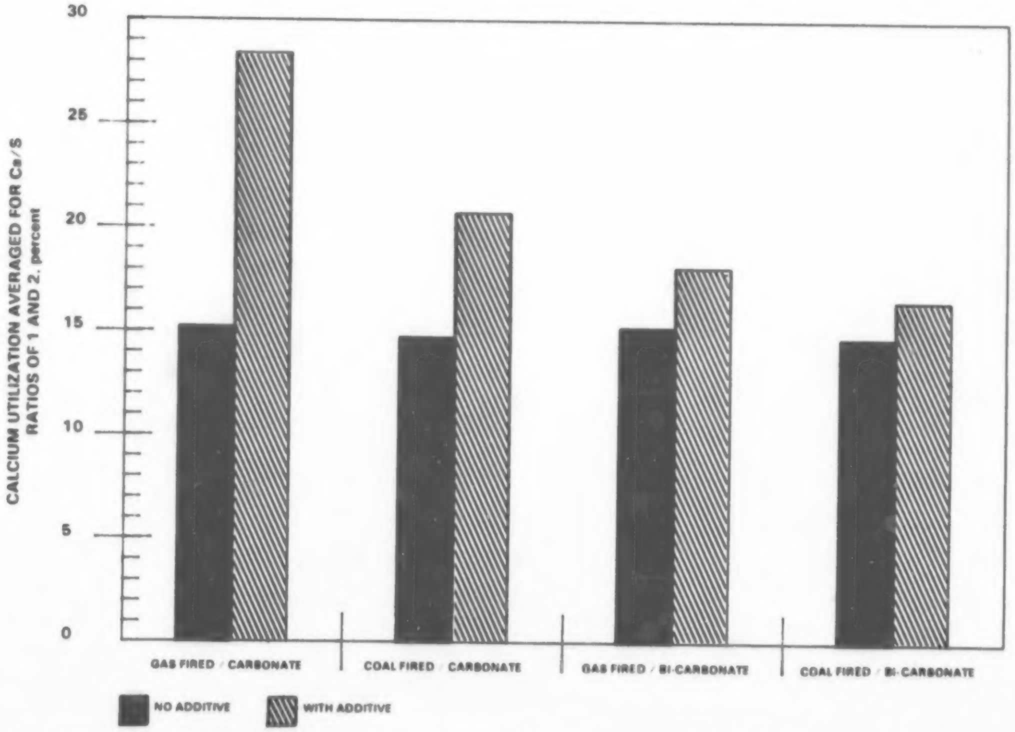

Figure 5. Performance of Vicron and Vicron with additives. Injection point is below burner.

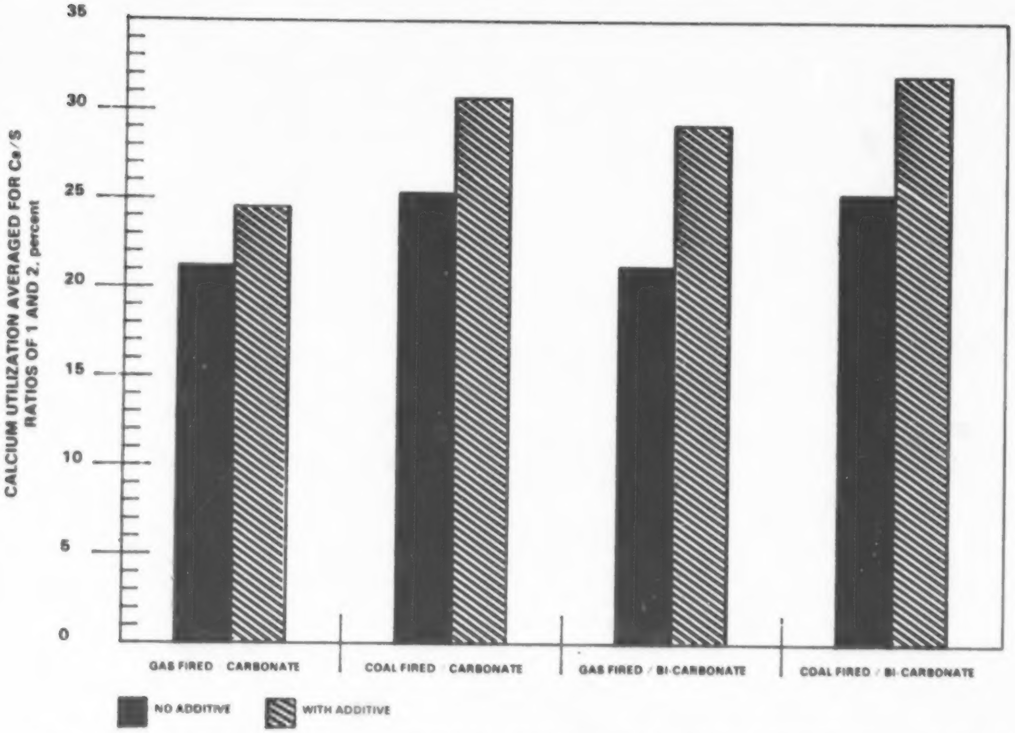

Figure 6. Performance of Genstar and Genstar with additives. Injection point is below burner.

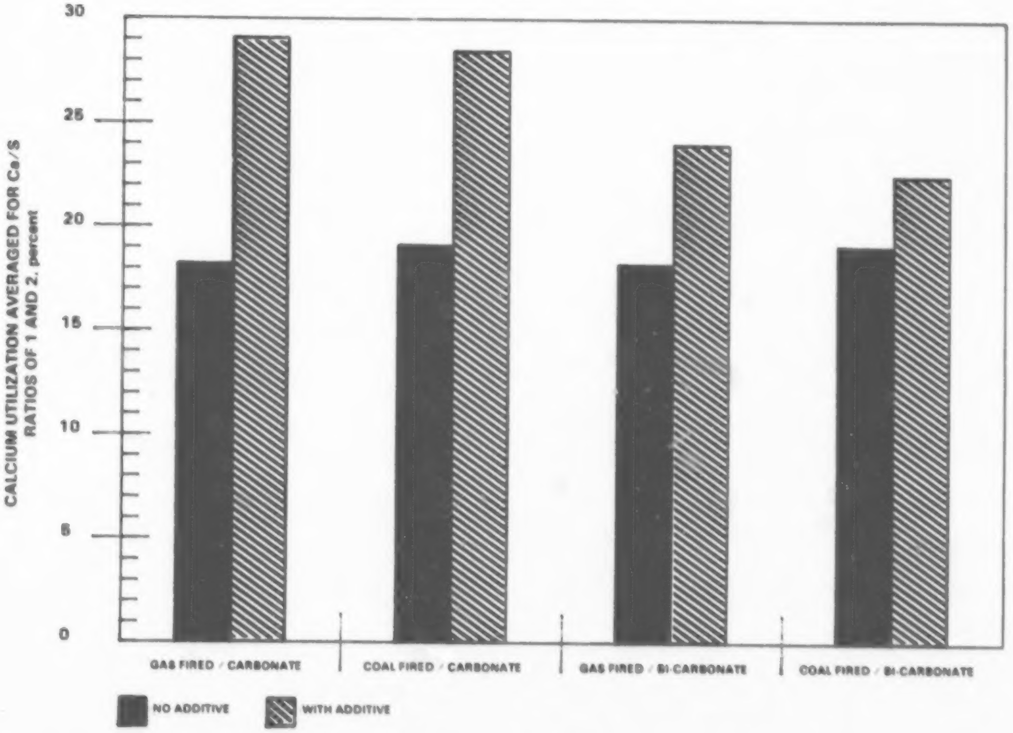

Figure 7. Performance of calcium hydroxide and calcium hydroxide with additives. Injection point is below burner.

Table 1

PITTSBURGH #8 COAL ANALYSIS SUMMARY
ON AN AS-RECEIVED BASIS

	December 1983	November 1983			Average of Three
Analysis	CTE	PENELEC	PENELEC	PENELEC	PENELEC
Moisture (%)	1.92	1.42	1.36	1.38	1.39
Ash (%)	7.53	7.50	7.52	7.50	7.51
Volatile (%)	36.73	37.31	37.21	37.16	37.23
Fixed Carbon (%)	53.82	53.77	53.91	53.96	53.88
Pyritic Sulfur (%)	0.85	0.38	0.40	0.39	0.39
Total Sulfur (%)	2.58	2.62	2.60	2.58	2.60
Btu/lb	13,746	13,490	13,478	13,500	13,489
MJ/kg	32	31	31	31	31

SESSION III: PILOT-SCALE DEVELOPMENT OF FURNACE INJECTION

Chairman, Michael McElroy, EPRI

PILOT-SCALE CHARACTERIZATION OF A DRY CALCIUM-BASED SORBENT SO_2 CONTROL TECHNIQUE COMBINED WITH A LOW-NO_x TANGENTIALLY FIRED SYSTEM

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ABSTRACT

A 380-kW_t (1.3 million Btu/hr) two-burner-level tangentially fired pilot-scale facility was used to characterize a dry calcium-based sorbent SO_2 capture technique combined with an offset auxiliary air low-NO_x burner with and without overfire air. Baseline tests using a conventional burner design, with and without overfire air, showed that the facility properly simulates full-scale uncontrolled and controlled NO emissions and furnace temperature histories. SO_2 test results with dry sorbent injection and the conventional burner were consistent in level and trend with limited field data. Efficiency, as determined by carbon monoxide, unburned hydrocarbon, and carbon in flyash levels, was good for all test conditions and consistent with field practice.

Dry sorbent SO_2 test results showed that SO_2 capture is increased by: (1) utilizing conventional rapid fuel/air mixing burners, (2) injecting sorbent away from the flame (i.e., not mixing sorbent with the fuel), (3) avoiding contact between ash and sorbent, and (4) holding sorbent in the sulfation temperature zone (i.e., 1,505 to 1,255K) as long as possible. In addition, fuel and sorbent type had a significant impact on SO_2 capture.

INTRODUCTION

Coal-fired tangential boilers produce 35 percent of the NO_x and consume, in Btu's, 45 percent of the fuel used in all coal-fired utility boilers (Reference 1). Since almost all of the sulfur contained in the coal appears in the flue gas as an oxide, the significant coal fuel usage of tangential boilers also makes them an important source of SO_x emissions.

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The significant contribution of coal-fired tangential boilers to national NO_x and SO_x emissions and the expected future increase in the number of these boilers make them candidates for emission control development. Demonstrating cost-effective NO_x and SO_x reduction technology for these boilers will provide regulatory agencies with additional emissions control options which could be exercised in the future to prevent environmental degradation.

A pilot-scale low-NO_x tangential burner, which incorporates auxiliary air angle offset relative to the primary fuel jets, has been tested; it shows significant promise in controlling NO_x below current levels. Tests in the EPA pilot-scale test facility have shown the potential of achieving NO_x emissions in the range of 90 to 130 ng NO_2 per J (0.2 to 0.3 lb NO_2 per million Btu) (Reference 2). This low-NO_x system has gas temperature and oxygen concentration histories which could benefit the dry sorbent SO_2 capture relative to conventional burners (Reference 3). With the low-NO_x burner, heat release is spread out in the furnace, thereby lowering peak temperatures; in conventional burner systems, high peak temperatures can possibly deactivate sorbent. Also, oxygen deficient zones are present in the low-NO_x system. In these zones, the sorbent could possibly capture sulfur as a sulfide rather than a sulfate. Sulfide capture could have reaction rate and product volume advantages over sulfate capture, which is the typical mode of capture in conventional burner systems.

Given the potential for good NO_x and SO_2 control, low-NO_x burner dry sorbent injection tests were performed to determine: (1) the feasibility of the low-NO_x burner to achieve high SO_2 capture through dry sorbent injection, (2) the influence of the injection system and combustor design variables on SO_2 control, and (3) the SO_2 emission performance of several fuels and sorbents.

Description of Conventional Coal-Fired Tangential Systems

Figure 1 illustrates the main features and flow patterns of a tangentially fired boiler. Fuel and air flow into the furnace through rectangular registers located in the four corners of the unit. As shown in Figure 1, the burner consists of a primary air register which introduces the fuel and a small fraction of the combustion air into the furnace. Surrounding the primary register is the annular air register, which contains a fraction of the secondary combustion air. The auxiliary air registers, above and below the primary and annular registers, contain the bulk of the secondary combustion air flow. The jets are inherently nonswirling and fuel/air mixing is slow, relative to front-wall-fired boilers.

The tangential alignment of the centerlines of the corner jets to the circumference of a circle in the center of the furnace promotes the formation of a large-scale vortex within the furnace. Ignition of the fuel is provided by impingement of hot burnt gases from laterally adjacent burners and large-scale internal recirculation of combusted gases. Because ignition occurs primarily on the vortex core side of the fuel jet (see Figure 1), combustion is asymmetric in the near-burner horizontal plane.

Pilot-Scale Development of a Low-NO_x Tangential System

Figure 2 presents a top and side view schematic of the low-NO_x system as installed in the EPA pilot-scale test facility (Reference 2). In this schematic, fuel-rich and fuel-lean zones in the firebox are identified. The major system features are:

(1) fuel directed at the conventional burner yaw angle* into the center of the furnace, (2) some secondary air introduced at the same yaw angle as the fuel, in an annular space surrounding the fuel jet, and (3) the rest of the secondary air directed along the wall at and above the fuel jet elevation. During operation, coal and primary air are injected into the furnace at roughly a 0° to 8° yaw angle with respect to the firebox diagonal. The primary air flow represents about 15 percent of the total combustion air. Surrounding the primary fuel jet is an annular passage in which some of the secondary combustion air is flowing.

The fuel jet initially burns on the jet boundaries in a diffusion flame manner. Since most of the fuel nitrogen evolves inside the oxygen-deficient jet, the initial NO_x formation is limited for the slow-mix diffusion burning of the jet.

As previously shown in Figure 2, a fraction of the combustion air is directed along the furnace walls. Since the wall air yaw angle is large (approximatey 45° for a square firebox), the wall air contributes significantly to the vortex swirl level. Because the wall jet places the air in a relatively aerodynamically quiescent region along the wall, it remains separate from the fuel in the center of the furnace for a longer period of time than if it was injected at some positive angle away from the furnace wall. In addition to large wall-air yaw angles, intermediate yaw angles have been tested which exhibit NO_x reduction benefits.

When the wall jets contain a significant fraction of the air flow needed to complete combustion, the center of the furnace at the fuel entry elevation operates with a deficiency of oxygen. Under these conditions, NO_x (previously formed during the initial diffusion burning) and any remaining fuel nitrogen evolved in the center of the furnace are decayed to molecular nitrogen by homogeneous and heterogeneous chemical processes. Since molecular nitrogen is relatively unreactive for NO_x formation in the fuel burnout zone, the decay processes in the center of the furnace produce low-NO_x levels in the stack. Eventually, the air directed along the furnace walls mixes with the oxygen-deficient vortex core gases and char, completing combustion.

Besides limiting NO_x production to the range 90 to 130 ng NO_2 per J (0.2 to 0.3 lb per million Btu), directing a fraction of the combustion air along the furnace walls maintains the walls under oxidizing conditions. This eliminates degradation of the metallic furnace surface by reducing gases. In addition, the iron in the ash deposits will be maintained in the ferric rather than ferrous form, thereby raising the ash fusion temperature and reducing the wall slagging potential.

PILOT-SCALE TEST FACILITY

The pilot-scale facility and instrumentation used in the combined low-NO_x/SO_x test program is a modification of the EPA multifuel furnace pilot-scale facility used on the prior EPA-sponsored coal-fired tangential system NO_x emissions control program (Reference 2). The facility was modified extensively to upgrade the modeling of full-scale multiple-burner-level tangential systems and thermal profile effects. These modifications were necessary to properly simulate NO_x emissions and dry sorbent SO_2 control of modern large-scale multiple-burner tangential systems modified for NO_x and SO_2 control.

The pilot-scale facility geometry used on this program is an approximate 1 to 14 scaling of an existing, modern-design Combustion Engineering tangentially fired boiler. The overall external height of the furnace is approximately 3.7 m (12 ft) and it is capable of firing coal or gas at rates up to 587 kW_t (2 million Btu/hr).

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*Yaw angle is defined as the angle the burner port centerline makes with the firebox diagonal. A typical yaw angle is 6° off the firebox diagonal.

The main firebox, or radiant section, is a refractory-lined chamber with a rectangular 1 m by 1.1 m (38 in. by 44 in.) cross section. Two levels of burners are situated at each corner. Each burner set includes primary air, annular air, and auxiliary air ports. Overfire air ports are also installed above the pair of burners at each corner. The primary air and annular air jets have a small degree of firing angle variability -- up to 8° from the firebox diagonal. All other air jets can be directed at angles from 6° to 37° away from the diagonal. Three nominal angles for the auxiliary jets, denoted conventional, intermediate, and air-on-wall, are 6°, 21°, and 37° away from the firebox diagonal, respectively. Auxiliary and overfire air jet velocity can be varied independently of air flowrate through the burners. Three sizes of auxiliary and overfire air ports can be interchanged to achieve major variations in combustion air velocity. Overfire air ports are located 0.38 m (15 in.) above the burner centerline.

Volumetric heat release and gas residence time in the radiant section are closely approximated between pilot and full scale. Realistic furnace-exit gas temperatures are achieved by low heat loss refractory linings in the main firebox and ash pit.

The facility is fully instrumented with continuous monitors to measure stack NO, SO_2, UHC, CO, CO_2, and O_2 gaseous concentrations, and thermocouples are placed at various locations throughout the furnace to monitor furnace wall and gas temperatures. In addition, suction pyrometers and gaseous and solid sampling probes can be inserted into the furnace at various locations in the radiant and convective sections to monitor in situ gas temperatures and gas and solid compositions.

SO_2 REDUCTION TEST RESULTS AND DISCUSSION

The goal of these tests was to characterize the effect of major parameters influencing dry sorbent injection SO_2 reduction in the tangentially fired system. Emphasis was placed on testing under the low-NO_x firing condition (auxiliary air angle at air-on-wall) to investigate the effectiveness of simultaneous NO_x/SO_2 control.

The major sorbent injection parameters studied in these tests included sorbent injection method and location, convective heat exchanger tube arrangement, load, excess air, flue gas recirculation (FGR), fuel type, and sorbent type. During the tests, medium velocity air jets were utilized and sorbent transport air flow was fixed at 22.7 kg/hr (50 lb/hr). All Ca/S ratios reported do not include the inherent calcium present in the coal.

Baseline SO_2 Reduction Test Results Summary

The objective of these tests was to determine if the conventional burner pilot-scale SO_2 reduction results were comparable in level and trend with past studies. The tests consisted of varying the major dry sorbent injection parameters, observing their trends and effects, and then, where appropriate, comparing them with past studies. All of the baseline SO_2 reduction tests were carried out with a conventional burner design in which the auxiliary air offset angle is equal to the fuel jet angle. The parameters investigated included calcium-to-sulfur ratio, excess air, load, sorbent injection location, sorbent type, and coal type. Coal properties and sorbent chemical compositions and sizes are given in Tables 1 and 2, respectively.

The test results for these parameters showed that the baseline SO_2 reduction trends were generally consistent with previous results. Also, based on comparisons with limited field data, the pilot-scale results reflect field experience. This comparison is encouraging evidence that the pilot-scale facility SO_2 reduction results can be used as a guide in assessing how SO_2 reduction performance would vary with design or operating conditions in a full-scale furnace.

In addition to SO_2 comparisons, controlled and uncontrolled NO emissions and temperature histories compared favorably with field levels. Efficiency, as determined by carbon monoxide, unburned hydrocarbon, and carbon in flyash levels, was good for all test conditions and consistent with field practice.

Conventional and Low-NO_x/SO_2 Reduction Test Results

The objective of these tests was to determine the impact of major NO_x-reduction methods (i.e., offset auxiliary air and overfire air) on the dry sorbent injection SO_2 reduction process. Various combinations of overfire air and auxiliary air offset angle were used in these tests. Overfire air sorbent injection, where sorbent was thoroughly mixed with the overfire air prior to injection, was utilized in these tests.

Figure 3 shows that with the conventional burner, overfire air NO_x control reduces sorbent SO_2 capture performance over the whole range of Ca/S values tested. As indicated on the figure, Illinois coal and El Dorado sorbent were used in these tests, and load and excess air were set at nominal values (390 kW and 20 percent, respectively). Next to the percent overfire air designation in Figure 3 is a string of four numbers separated by slashes which denote the percent of the total combustion air flowing in the primary, annular, auxiliary, and overfire air ports, respectively. For subsequent figures, these designations will appear in the figure conditions table aligned with "air splits." In addition, the string of three numbers aligned with "convective" in the conditions table on the figure denotes the number of coolant loops in, respectively, the first three tube banks in the furnace conventive heat exchanger section. Except where noted, these conditions were maintained for all of the tests reported.

The test results in Figure 4 show that offsetting the auxiliary air to intermediate and air-on-wall angles with overfire air, further reduces SO_2 capture relative to the conventional burner with overfire air case. From both Figures 3 and 4 it is apparent that lowering NO_x, through overfire air addition alone and in combination with offset auxiliary air, reduces sorbent SO_2 capture effectiveness.

The varying levels of SO_2 reduction are possibly caused by the differences in fuel-components-air-sorbent contact (or, in general terms, "mixing"). Mixing pattern differences are a direct result of the three different auxiliary air angles and overfire air addition. Besides mixing, the different air injection approaches alter residence time distribution in the furnace. Additionally, the low-NO_x systems control NO_x by delaying fuel/air mixing and thereby stretching out the furnace heat release. The presence of local high-temperature flames in the sorbent injection zone could be detrimental to sorbent activity and therefore SO_2 capture.

Even though sorbent SO_2 capture was not optimal with the low-NO_x techniques tested, the offset auxiliary air low-NO_x burner was utilized on all further sorbent injection tests to determine the impact of design and operating parameters on a combined NO_x and SO_2 control system.

Effect of Sorbent Injection Method and Location

The objective of this test sequence was to determine the effect of sorbent injection method and location on SO_2 reduction with the offset auxiliary air low-NO_x burner. Figure 5 shows the effect on SO_2 reduction of injecting sorbent in the overfire, lower auxiliary (bottom), and primary air ports. In these tests, the sorbent was thoroughly mixed with the air flow prior to injection through the air ports into the furnace. The SO_2 reduction results show that overfire air sorbent injection produced SO_2 reduction similar to, but slightly better than, lower auxiliary air sorbent injection. Primary air injection of sorbent consistently gives the lowest SO_2 reduction levels. With primary air injection, the sorbent particle is expected to be in immediate contact with devolatilizing and burning fuel and therefore may deactivate due to high peak temperatures and ash contacting. This may be responsible for the lower SO_2 reduction levels for primary air sorbent injection presented in Figure 5.

SO_2 reduction results for probe sorbent injection 0.3 m (12 in.) above and 0.2 m (8 in.) below the burner zone were also obtained. The sorbent was injected upward into the center of the furnace through a 13-mm (1/2-in.) diameter nozzle. The SO_2 reduction levels for the two probe injection locations were found to be similar to the overfire air and lower auxiliary air port injection test results. Only primary air injection of sorbent gave reduced SO_2 capture. A possible explanation for such differences is the sorbent/fuel-components contact. Sorbent injection through overfire air, lower auxiliary air, and the water-cooled probe all provide a delay in contact of sorbent particles and fuel components. Such mixing is probably accomplished downstream of the hot primary combustion zone and outside of the flames, where gas temperatures are cooler. Sorbent injection through the primary ports should result in the immediate contact of burning fuel and sorbent in the high-temperature flame zones. The proximity of the fuel components (including ash) and sorbent, at high temperatures, may result in sorbent deactivation and therefore reduced SO_2 capture levels.

The similarity of SO_2 reduction levels (except for sorbent injection through primary air) suggests that, regardless of sorbent injection location, the bulk of SO_2 capture may be taking place farther downstream in the furnace. If sulfur is being captured as SO_2, equilibrium constraints under typical combustion conditions dictate that sorbent/gas temperatures need to be below 1,500K (2,300°F) for capture to occur. This would support the postcombustion zone capture of SO_2, since radiant section gas temperatures are typically above 1,500K (2,300°F). To approximately locate the zones of sulfur/sorbent reaction and test the above postcombustion zone SO_2 capture speculations, sorbent was injected into the furnace's upper radiant and convective sections using a single-point water-cooled injection probe, as in the center of the furnace injection tests discussed above.

Injecting sorbent into the convective section from the radiant section or into the convective section counter to the gas flow gave results similar to all injection locations, except the primary air injection location and ceiling-down injection location. The reason ceiling-down injection of sorbent produces low-SO_2 reduction levels is not understood. It could be speculated that ceiling-down injection directs some of the sorbent into flame zones, where deactivation of the sorbent occurs. However, no data are available to support this conjecture.

The similarity of most of these results, for different injection locations, implies that stable SO_2 capture is taking place in the convective section where temperatures are below 1,533K (2,300°F) and that there is no significant capture occurring in the radiant section of the furnace. Even if there is sulfur capture in the radiant section, the calcium-sulfur product may be quickly dissociated.

All of the previously mentioned SO_2 reduction test results using the water-cooled sorbent injection probe were carried out with a single-point 13-mm (1/2-in.) diameter outlet nozzle. The effect of using different nozzle sizes was also investigated. These results showed that nozzle size, and thereby nozzle exit velocity, had very little effect on SO_2 reduction. Apparently, in the relatively small furnace, sorbent/gas mixing is not a major problem.

Effect of Furnace Load, Convective Heat Transfer Tube Arrangements, and FGR

Furnace load, convective heat transfer tube arrangement, and FGR are parameters that influence dry sorbent injection by affecting primarily the temperature/residence time profile, and mixing patterns in the cases of furnace load and FGR changes, and possibly combustion chemistry in the case of FGR. Temperature profiles were measured to help explain the effect of FGR and load on sorbent SO_2 capture.

The test results in Figure 6 show that lowering load significantly improves SO_2 reduction. The improved SO_2 reduction can be related to a modified thermal history as load is reduced. The temperature profiles for normal (390-kW_t) and low-load (300-kW_t) cases are considerably different. In the temperature zone of 1,255 to 1,505K (1,800° to 2,250°F), the normal-load case provides approximately 1 sec residence time, while the low-load case provides about 4 sec. Such large differences in residence time in the sulfation temperature zone may account for the significant improvement in SO_2 reduction as load is reduced.

The effect of FGR on SO_2 reduction was determined by pumping filtered flue gas out of the baghouse and back into the furnace through the overfire air ports. Despite some degree of scatter in the data, the test results in Figure 7 show that the addition of FGR improves SO_2 reduction. This trend was expected because FGR addition should cool the combustion products to create a more favorable temperature/residence time profile for sorbent-SO_2 reactions. Testing showed that the addition of FGR substantially lowers the entire thermal profile of the furnace, leading to the doubling of residence time in the temperature range of 1,355 to 1,505K (1,800° to 2,250°F), compared to the case with no FGR.

As another check of the effect of temperature history on sorbent capture, three different convective heat transfer tube arrangements were tested. By altering just the convective tube arrangements, mixing and heat release patterns in the lower furnace were not disturbed. Therefore, through this test approach, the significance of convective section temperature history on SO_2 capture could be clearly shown. As anticipated, lowering the convective section temperature into the sulfation temperature zone (less than 1,505K (2,250°F)) for a significant length of time increases SO_2 capture. Greater than factors of two in capture were observed between different heat transfer tube arrangements. These results supported the low load and FGR tests and clearly showed the importance of convective section temperature history, independent of radiant section conditions.

To summarize the temperature history results, Figure 8 presents the SO_2 reduction obtained for a given amount of residence time in the temperature range between 1,255K and 1,505K (1,800°F and 2,250°F). Temperatures were varied by changes in load and convective heat exchange tube arrangements. For nominal conditions of Illinois coal, El Dorado sorbent at a Ca/S of 2, probe injection 0.3 m (12 in.) above the burners with the baseline low-NO_x firing conditions, the SO_2 trend shows a clear increase of capture with increases in residence time in the temperature range conducive to sulfate formation. It should be noted that FGR test results are also consistent with these trends. This trend with residence time at temperature is evident for both El Dorado limestone and dolomite, with medium and coarse dolomite showing better capture for equivalent residence time.

Effect of Fuel Type

Four fuels were tested for sulfur capture with El Dorado limestone. Properties of these fuels are presented in Table 1. Two noteworthy features about the fuels are their inherent levels of sulfur (ranging from 0.6 percent in North Dakota lignite and Utah bituminous to 3.7 percent in Illinois bituminous) and their heating values (ranging from approximately 24,207 J/g [10,407 Btu/lb] for the lignite up to 29,554 J/g [12,760 Btu/lb] for the bituminous coals). SO_2 reduction test results presented in Figure 9 for the three bituminous coals fired under nominal conditions show that high-sulfur Illinois coal gives the highest capture, while the lowest capture was obtained with the moderately high-sulfur Indiana coal. Low-sulfur Utah coal gave an intermediate level of capture.

The North Dakota lignite tests were conducted at a reduced load (70 percent of nominal) consistent with lignite fuels firing intensity practice. Under these conditions, more SO_2 capture is obtained from Illinois coal (42 percent at Ca/S = 2) than from the lignite (32 percent at Ca/S = 2).

SO_2 reduction from a "dirty" fuel, Illinois coal, was compared to that of a "clean" fuel, natural gas, doped with an equivalent concentration of sulfur in the form of hydrogen sulfide (H_2S). Compared to the coal, a factor of two greater sulfur capture was found for doped gas. It was speculated that either there is some aspect of homogeneous gas-phase combustion which enhances SO_2 reduction or a feature of heterogeneous coal combustion which inhibits reduction.

A set of tests was performed to determine if the mineral matter in coal was inhibiting sulfur capture. For these experiments, two mixtures of El Dorado limestone and Utah coal ash were prepared and injected into the doped-gas fireball.

The mixtures were blended to produce flue-gas-ash concentrations which would correspond to a high- and a low-ash fuel. At limestone/ash injection rates which equated to calcium sulfur ratios of 2.0, the low-ash mixture simulated a fuel which would be 3 weight percent ash, and the high-ash mixture simulated a 13 percent ash fuel.

In Figure 10, the results of these tests show that, for a calcium/sulfur stoichiometry of 2.0, the pure limestone captured 19 percent of the SO_2, while the low- and high-ash blends captured 12 and 8 percent, respectively. These results indicate that Utah coal ash has a detrimental effect on limestone/sulfur reactivity. It can be speculated that the ash material, through either a gas-to-solid or solid-to-solid process, combines with the sorbent to reduce its overall activity for sulfur capture.

Effect of Sorbent Type

Five sorbents were tested under baseline firing conditions with Illinois coal. Properties of these sorbents are presented in Table 2. Test results presented in Figure 11 show that sulfur capture varied significantly, from 5 to 29 percent (at Ca/S = 2), with the sorbents ranked in order of increasing capture as follows: marl, vicron, chalk, El Dorado, and dolomite.

CONCLUSIONS

Pilot-scale tests showed that delaying the fuel/air mixing, through OFA and offset-auxiliary air with OFA low-NO_x approaches, reduces dry sorbent injection SO_2 capture effectiveness.

Extensive dry sorbent injection tests with the low-NO_x offset auxiliary burner (i.e., air-on-wall) without OFA showed that:

- Temperature history, as affected by changes in load, convective tube arrangements, and flue gas recirculation, has a very strong impact on sorbent SO_2 capture. Sorbent capture appears to be proportional to residence time in the 1,505 to 1,255K (2,250°F to 1,800°F) temperature band.
- Adding ash mineral matter to a doped gas flame significantly reduces sorbent SO_2 capture.
- Injection of sorbent into the primary air port gives consistently lower SO_2 reduction, presumably by ash interaction with the sorbent.
- Sorbent injection at all other locations (lower auxiliary air, OFA, probe center injection above and below the burners, and probe-roof convective and counter convective), except roof-down probe injection, gave similar and better SO_2 reduction than primary injection.
- Downward sorbent injection from a probe in the center of the roof gives SO_2 reductions similar to primary injection.
- For the parameter ranges tested, sorbent injection velocity has an insignificant effect on SO_2 reduction in the relatively small scale furnace.
- Fuel and sorbent type have a significant effect on SO_2 reduction.

These test results strongly suggest the following path to optimum sorbent SO_2 capture:

- Inject the sorbent downstream in the upper furnace or convective section to avoid any sorbent deactivation by either high peak temperatures or by fuel ash.
- Hold sorbent in the active sulfation temperature zone as long as possible through modification of the convective section heat transfer arrangement, load or flue gas recirculation.
- Use sorbents which are resistant to deactivation through ash interaction and high temperatures.

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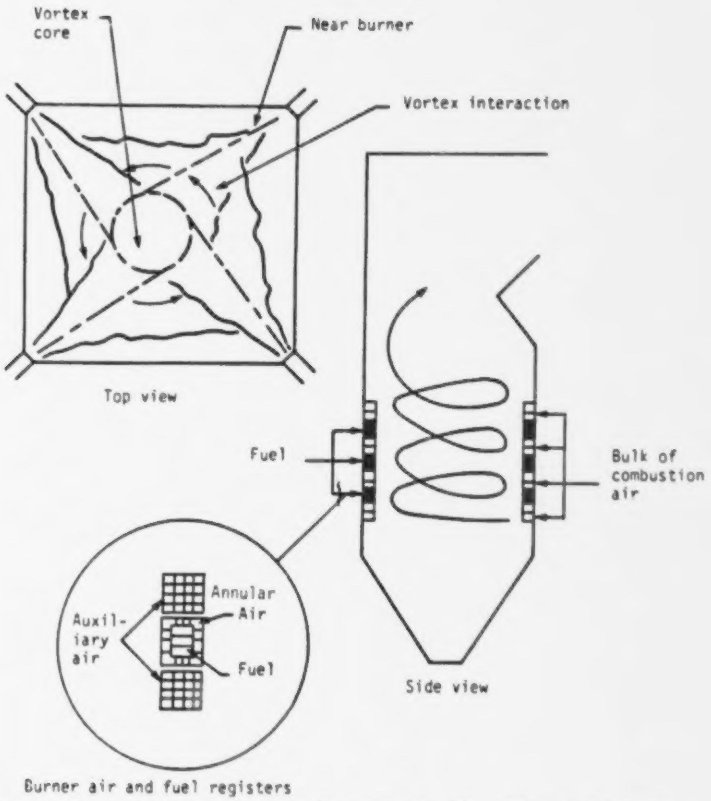
Vortex core
Near burner
Vortex interaction
Top view
Fuel
Bulk of combustion air
Annular Air
Auxil-iary air
Fuel
Side view
Burner air and fuel registers

Figure 1. Schematic of Tangentially Fired System

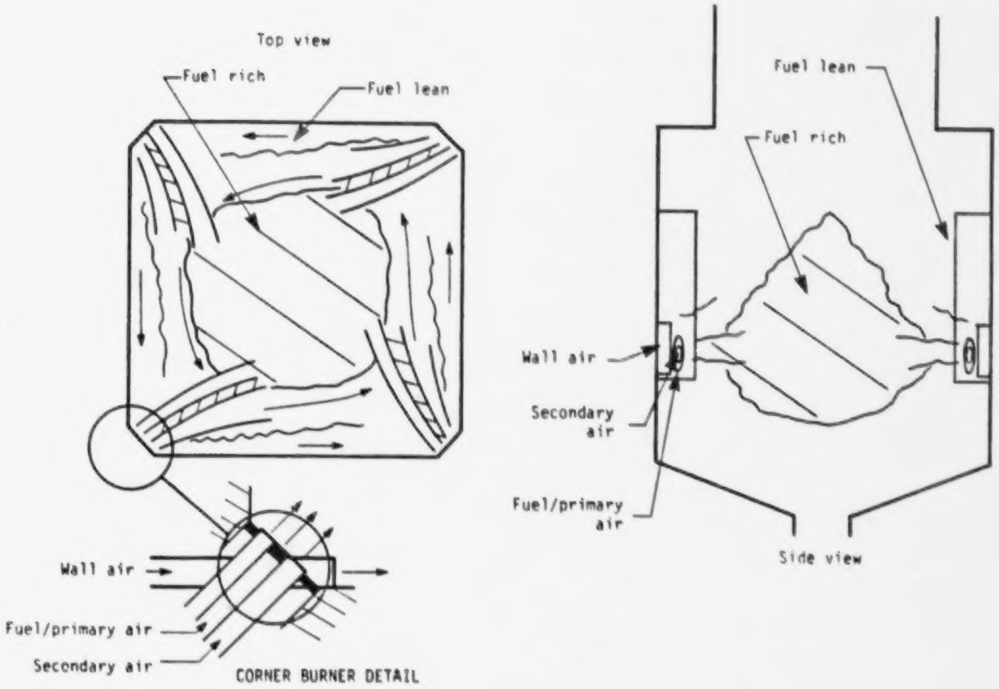
Top view
Fuel rich
Fuel lean
Wall air
Fuel/primary air
Secondary air
CORNER BURNER DETAIL
Fuel lean
Fuel rich
Wall air
Secondary air
Fuel/primary air
Side view

Figure 2. Low-NO_x Air-on-Wall Concept Schematic

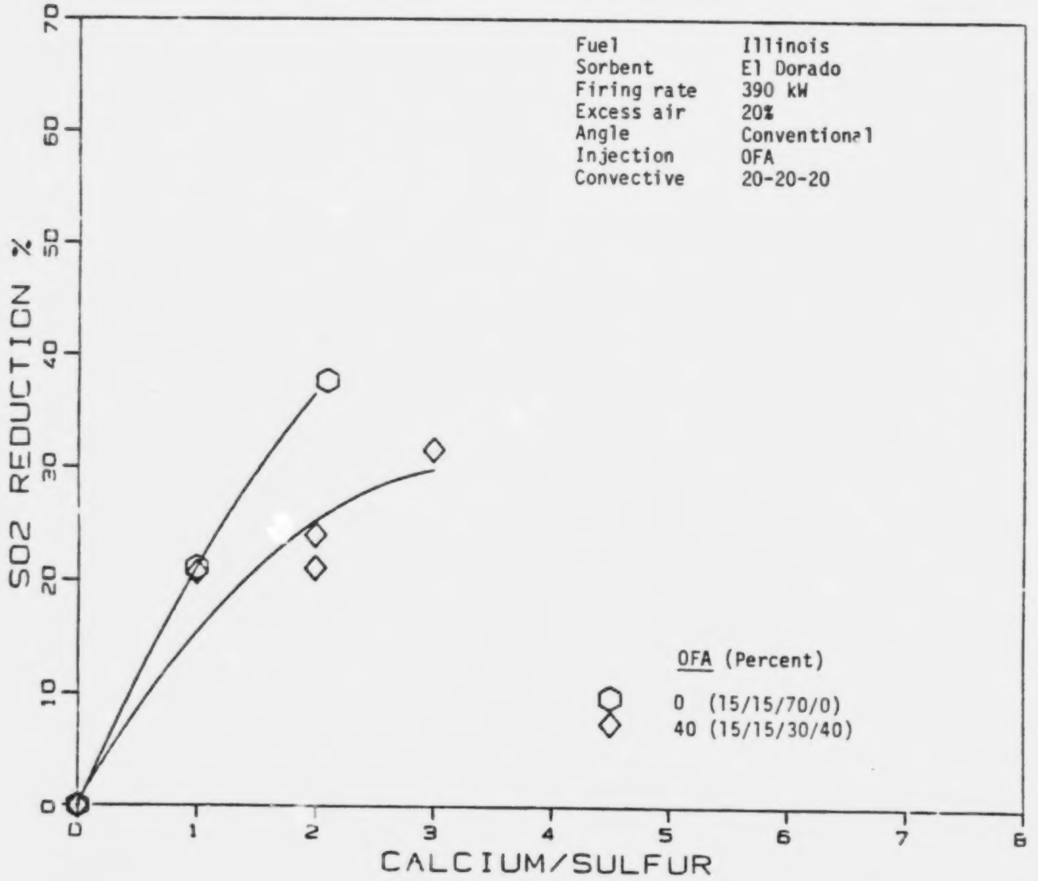

Figure 3. Effect of Combustion Air Distribution with Overfire Air Sorbent Injection on SO_2 Reduction

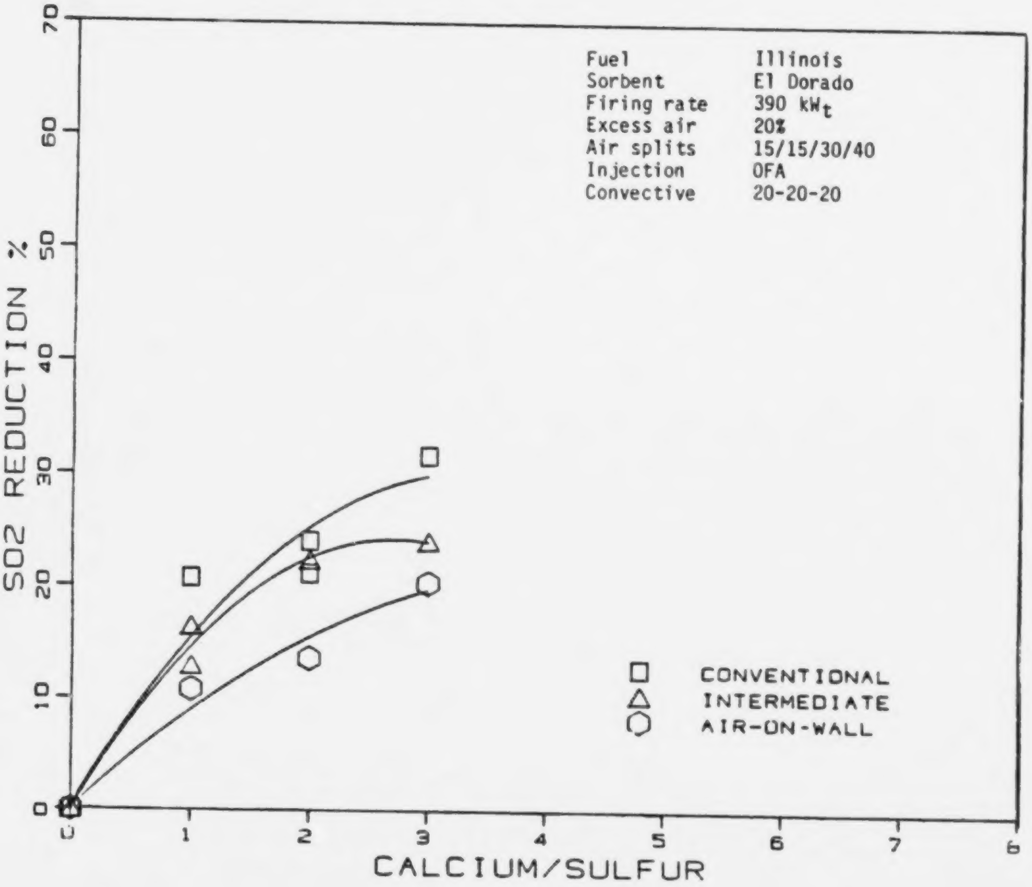

Figure 4. Effect of Auxiliary Air Angle with Overfire Air Sorbent Injection on SO_2 Reduction

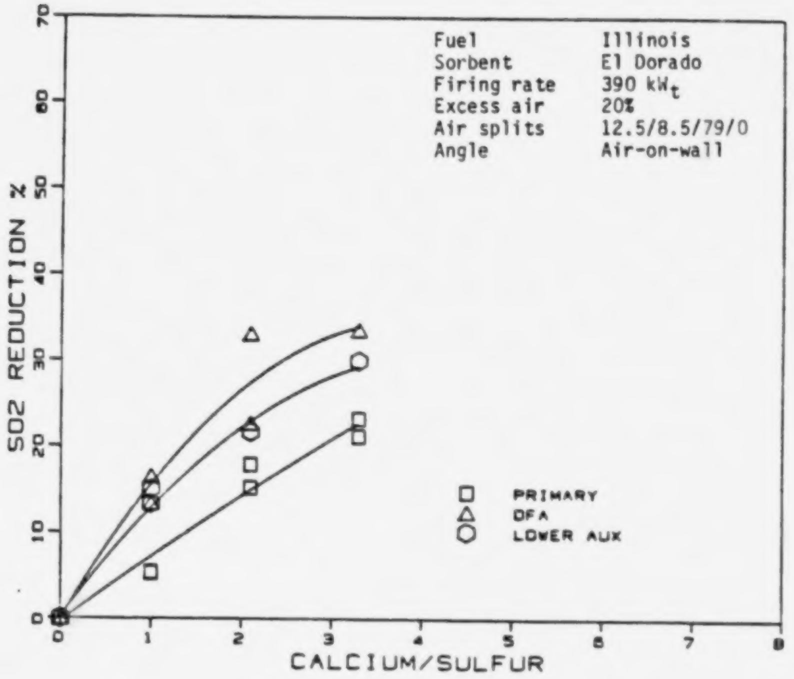

Figure 5. Effect of Sorbent Injection Location on SO_2 Reduction

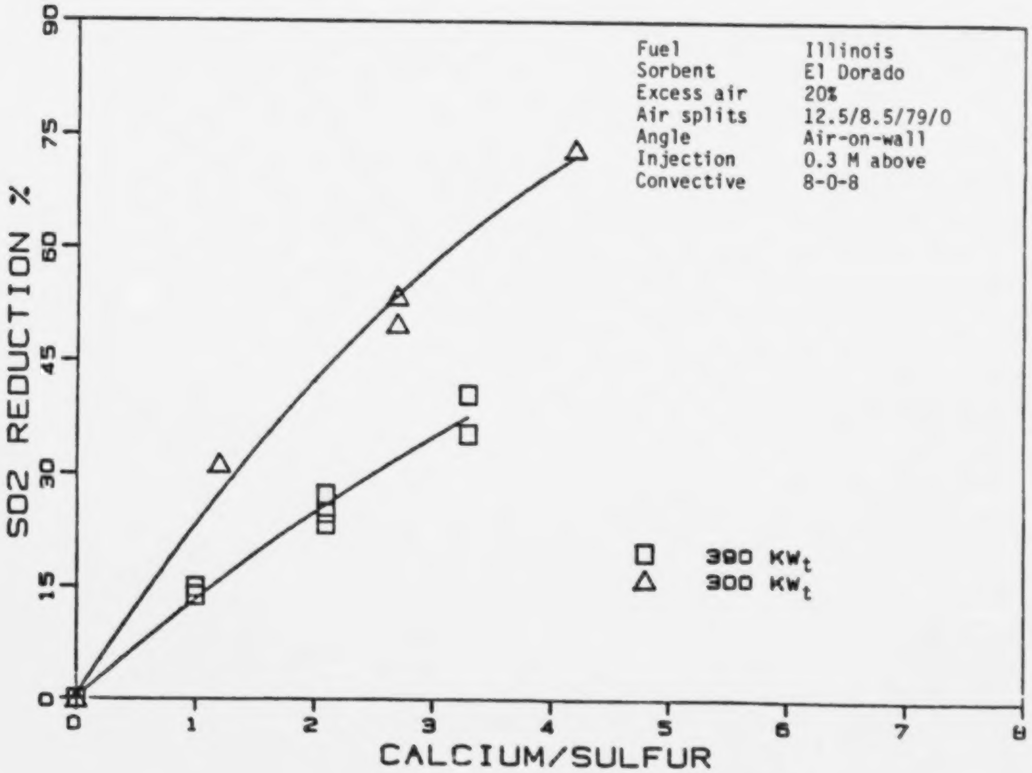

Figure 6. Effect of Firing Rate on SO_2 Reduction

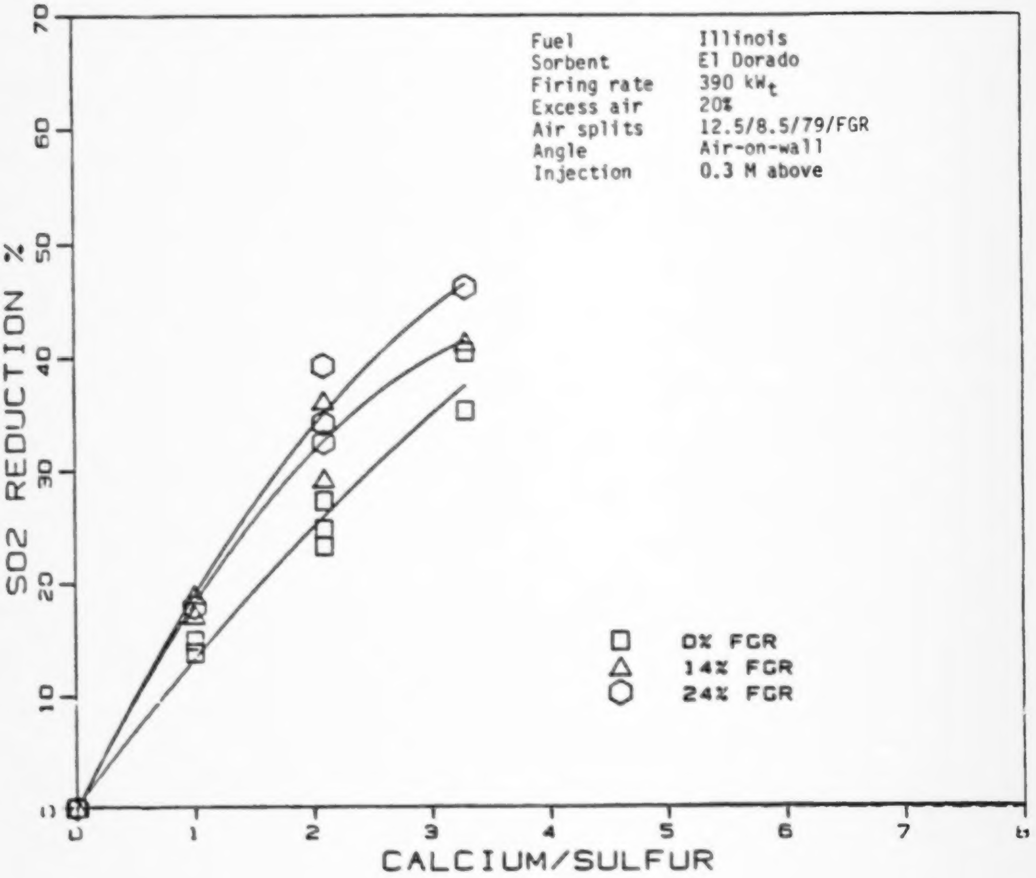

Figure 7. Effect of Flue Gas Recirculation on SO_2 Reduction

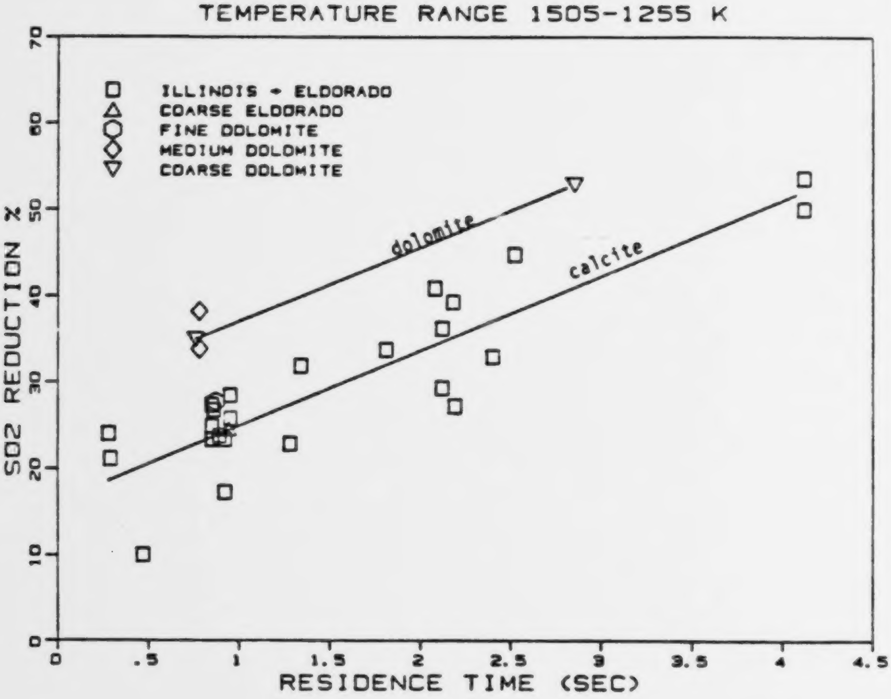

Figure 8. Effect of Residence Time in the 1,505 to 1,255K (2,250° to 1,800°F) Temperature Band at Ca/S of 2 on SO_2 Reduction

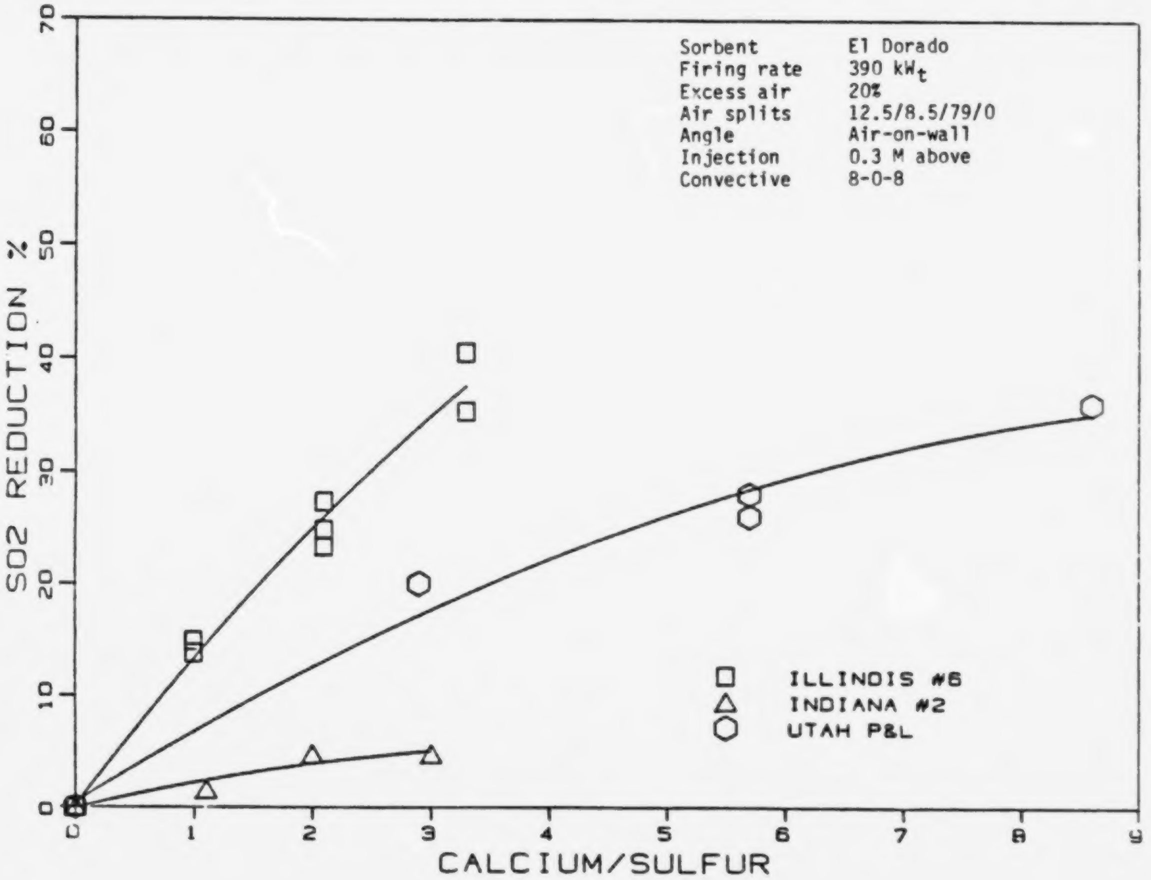

Figure 9. Effect of Fuel Type at Nominal Load on SO_2 Reduction

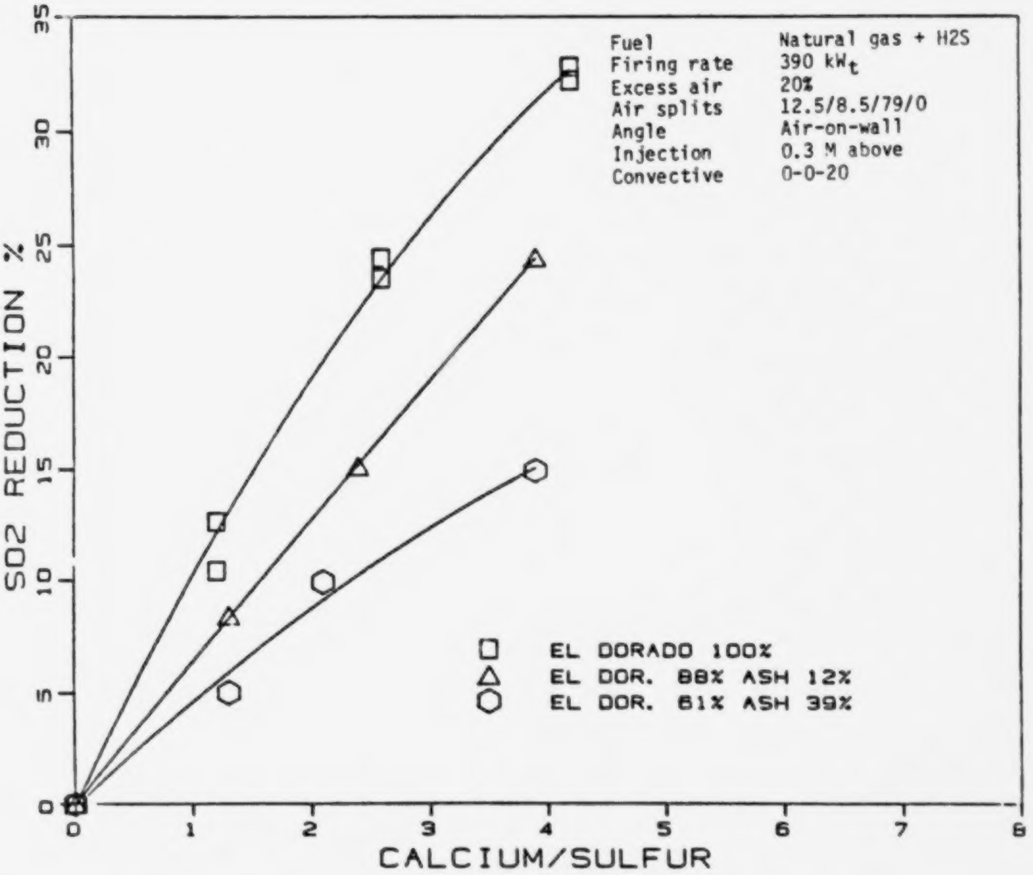

Figure 10. Effect of Ash Additive on SO_2 Reduction

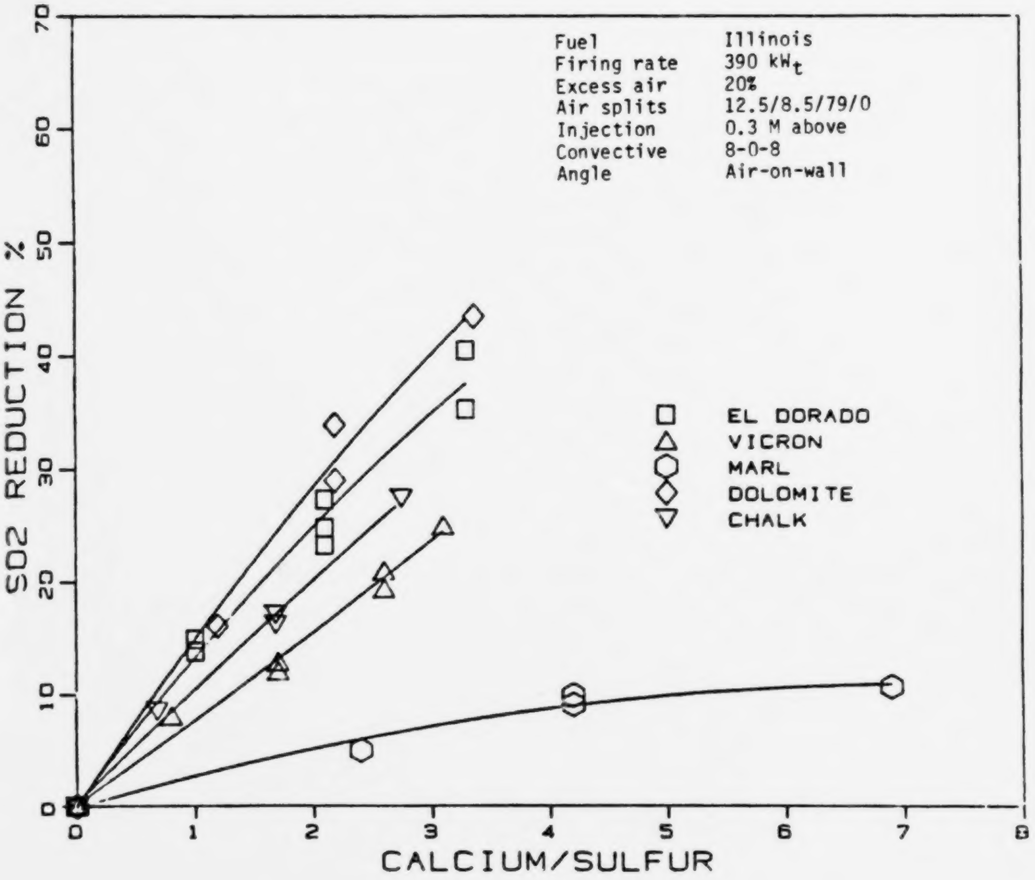

Figure 11. Effect of Sorbent Type on SO_2 Reduction

Table 1

TEST COAL PROPERTIES

Ultimate Analysis (as received)	Illinois Bituminous	Utah Power & Light Bituminous	North Dakota Lignite	Indiana Bituminous
C	62.0	62.5	43.6	70.7
H	4.5	4.6	3.0	4.7
O	7.6	9.8	13.4	8.7
N	1.0	1.1	0.1	1.3
S	3.7	0.6	0.6	1.3
Ash	11.5	18.0	8.8	10.3
H_2O	9.6	3.5	30.6	3.1
Heating value (Btu/lb)				
Dry	12,325	11,516	10,407	12,760
Wet	11,138	11,116	7,222	
Proximate analysis (as received)				
Volatile	36.5	36.9	29.7	34.3
Fixed carbon	42.4	41.7	30.9	52.3

Table 2

SORBENT CHEMICAL COMPOSITION AND SIZES

Sorbent Properties	El Dorado Limestone, El Dorado, California	Pfizer Dolomite, Gibsonburg, Ohio	Vicron (Pfizer) Limestone, Lucerne Valley, California	Michigan Marl, Hopkins, Michigan	Kansas Chalk, Jewell, Kansas
$CaCO_3$ (%)	98.0	54.3	97.0	92.2	82.8
$MgCO_3$ (%)	0.9	45.3	1.6	6.7	0.9
Particle size	99.8%-325 mesh	99%-325 mesh 88%-200 mesh 25%-200 mesh	99%-325 mesh	--	99%-325 mesh

BOILER SIMULATOR STUDIES ON SORBENT UTILIZATION FOR SO_2 CONTROL

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ABSTRACT

A 300 kW Boiler Simulator Furnace was used to investigate the influence of combustion and sorbent parameters on the effectiveness of dry sorbent injection for SO_2 control under conditions typical of current utility practice. Extensive characterization studies were conducted to investigate the role of boiler thermal history on capture effectiveness for limestones, dolomites, and slaked limes. Data were also obtained for high surface area sorbents (produced by pressure slaking) and for promoted sorbents (produced by the addition of appropriate metallic additives) as a function of thermal environment, sorbent injection location, calcium to sulfur molar ratio, and SO_2 partial pressure. In general the results show that captures in excess of 50% at a Ca/S ratio of 2.0 can be achieved by several alternative methods. The experimental studies were supported by theoretical calculations using grain and pore models which combined consideration of the heterogeneous chemical reaction and diffusion processes.

INTRODUCTION

Sulfur capture by calcium based sorbent has been the subject of much research over the last two decades(1-4). Furnace injection was tried and abandoned because of poor performance which was attributed(1) to a combination of poor sulfur capture because of decreased sorbent activity due to dead burning at furnace temperatures and inadequate dispersion of the sorbent throughout the combustion gases. Interest in the technique was revived when pilot scale studies at EER indicated that higher sulfur captures could be achieved under low NO_x combustion conditions. The need to develop a low cost, retrofittable SO_x control technology and reduced performance goals have caused additional interest in the limestone injection concept. LIMB, Limestone Injection Multistaged Burners, was coined to emphasize that simultaneous NO_x/SO_x control could be achieved by using limestone injection in conjunction with a distributed mixing burner.

When the sorbent is initially injected into the high temperature combustion zone, calcination occurs and CO_2 or H_2O is evolved according to the following reactions:

$$CaCO_3 \xrightarrow[770]{\Delta} CaO(s) + CO_2(g)$$

$$MgCO_3 \xrightarrow[340]{\Delta} MgO(s) + CO_2(g)$$

$$Ca(OH)_2 \xrightarrow[370]{\Delta} CaO(s) + H_2O(g)$$

In the case of limestones, structural rearrangement takes place as the CO_2 is being evolved because the crystal structure of the carbonate (rhombohedral) differs from that of the oxide (cubic). After the calcination process occurs, sites for recrystallization of the oxide are well dispersed so that localized crystallites, or grains, are formed with a pore structure between them. Overall calcination rates have been well documented by Hyatt et al.(5), Borgwardt(6,7), and Coutant et al.(2). Particle heat-up appears to occur very rapidly (c.a. 50 ms) after the particle is mixed with the hot gas stream and, at typical industrial combustion temperatures, the overall calcination process appears to be essentially complete in less than 200 ms. The calcination conditions, particularly temperature and CO_2 partial pressure, influence the ultimate porosity and grain size. Extended exposure to high temperature causes the grains to coalesce (sinter) because the highly mobile oxide units quickly fill in the gaps where grain boundaries (or contact points) occur. This results in larger grains, with lower surface area.

Once the sorbent particle is calcined to CaO, it can react with the available sulfur species to form calcium sulfate. The overall reaction for sulfation is:

$$SO_2 + \tfrac{1}{2}O_2 + CaO = CaSO_4$$

but the exact mechanism for this reaction is not known. It may involve an initial formation of calcium sulfite or result from a reaction of sulfate ions with CaO. The overall reaction system has been studied extensively by Borgwardt(6), Ishihara(8), and others(9,10).

This paper describes the results from a combined experimental and theoretical study to investigate the influence of combustion and sorbent parameters on the effectiveness of dry sorbent injection for SO_2 control under conditions typical of current utility practice. A 300 kW Boiler Simulator Furnace was used to investigate the role of boiler thermal history, sorbent injection location, calcium to sulfur molar ratio, and SO_2 partial pressure on capture effectiveness with limestones, dolomites, and slaked limes with and without metallic promoters. The experimental studies were supported by theoretical calculations using grain and pore models which considered both the heterogeneous chemical reaction and the relevant diffusional processes.

EXPERIMENTAL SYSTEMS

All of the data presented in this paper were obtained with the 300 kW Boiler Simulator Furnace (BFS) which is illustrated in Figure 1. The facility consists of two main sections; a refractory-lined vertical radiant tower 0.56m in diameter by 5.8m tall with multiple access ports, and a horizontal convective section containing air-cooled heat exchangers. The BSF can be used to simulate a wide range of time/temperature profiles by positioning water-cooled panels or rods appropriately in the radiant section.

The facility utilizes a Distributed Mixing Burner (DMB) which down-fires coal or natural gas. Two preheated air streams, swirl and axial, are supplied to the burner, and four external staging ports located around the burner allow tertiary air injection. NO_x levels are minimized with the DMB due to the fuel-rich core that is produced in the flame zone.

For the natural gas studies, H_2S was injected at the burner to simulate the sulfur content of coal. All of the sorbents were fed from a calibrated, twin-screw volumetric feeder and injected at the burner with pulverized coal or natural gas, or injected downstream at section 6 in the radiant section.

Exhaust gas samples were withdrawn at sample port 10B (temperature approximately 1200 K) with a stainless-steel, water-jacketed probe and analyzed using standard continuous instrumentation for NO, CO, CO_2, and O_2. SO_2 samples were pulled through the phase discrimination portion of the probe which separated any sorbent particles from the gas stream. The SO_2 samples were then carried via a heated sample line to a permeation dryer and on to a Dupont non-dispersive ultraviolet SO_2 analyzer.

MODEL DESCRIPTION

Two sulfur capture models were used for data interpretation and experimental planning in this work. Both models assume that the sorbent has been fully calcined prior to the onset of the sulfation reactions; the models differ primarily in the manner in which they view the internal structure of the calcined sorbent particle. The first, a grain model, was developed by G. D. Silcox and D. W. Pershing at the University of Utah and is based primarily on the concepts of Hartman and Coughlin(11), Pigford and Sliger(12), and Hartman and Trnka(13). This model treats the sorbent particle as an agglomeration of tiny, non-porous spherical grains separated by voids. Alternatively, the pore model, developed by W. Clark and co-workers at EER, treats the sorbent particle as a single unit penetrated by cylindrical pores of varying sizes and is based on the work of Bhatia and Perlmutter(10) and others(9,14).

In both models the sulfation reaction is assumed to occur at the internal surface of the particle. As the reaction proceeds the product layer of calcium sulfate is formed. For a molecule of SO_2 to be captured by a sorbent particle it must overcome four resistances in series:

1. Boundary layer diffusion. SO_2 must diffuse from the free stream through the boundary layer around the particle.
2. Diffusion through macropores. SO_2 must diffuse through the internal particle structure.
3. Diffusion through the product layer. An SO_2 species must diffuse through the calcium sulfate product layer to reach unreacted CaO.
4. Surface reaction. The heterogeneous reactions forming $CaSO_4$ take place at the $CaO/CaSO_4$ interface.

The governing differential equations were obtained from material balances on the particle and gas stream. Both models assume that the intrinsic kinetics of $CaSO_4$ formation are zero order with respect to SO_2, that the CaO grains react by a shrinking core model, and that the MgO grains do not react. The intrinsic kinetic and product-layer diffusion rate-constants were obtained by fitting the fundamental work of Borgwardt(6) in the manner described by Hartman and Coughlin (11).

SYSTEM OPTIMIZATION

One phase of the work recently completed on the BSF focused on the influence of the boiler design/sorbent injection parameters on overall SO_2 capture. These studies included consideration of overall excess air, burner stoichiometry, radiant zone heat removal rate, burner swirl, general sorbent injection location (burner versus downstream), importance of sorbent premixing with fuel, and impact of low NO_x operation. The results of these studies indicated that the parameters which were most critical for the optimization of sorbent utilization were sorbent injection location and the time/temperature history between injection and 1200 K. These effects are discussed in detail in the following sections.

SORBENT INJECTION LOCATION

Figure 2 summarizes results obtained on the impact of sorbent injection location with a typical limestone and slaked lime. These data indicate that the SO_2 capture increased approximately linearly with increasing calcium to sulfur ratio, and higher capture was achieved with downstream injection at approximately 1500 K (2250°F) for both sorbents. These results agree well with the early work of Coutant et al.(15) who reported an optimum injection temperature of 1475 K. Figure 2 indicates that the slaked lime was more sensitive to injection location than the limestone, and that is typical of results with other calcium hydroxide materials. The desirability of downstream injection shown in Figure 2 is typical of the trends obtained with a wide variety of other sorbents with both gas-and coal-firing under both favorable and highly quenched thermal conditions.

Figure 3 illustrates the impact of varying the sorbent injection location on the key parameters controlling SO_2 capture. The top half of this figure shows the gas temperature measured during the experiments reported in Figure 2 as a function of residence time. These temperature measurements were obtained with a suction pyrometer and indicate that sorbent particles injected in the burner zone experienced peak temperatures in excess of 1700 K while the particles injected downstream cool rapidly from 1500 K. The bottom half of Figure 3 shows the influence of varying the point of sorbent injection (plotted in terms of residence time) on the surface area of the calcined sorbent (without SO_2 present). Downstream injection greatly enhances the surface area available for subsequent sulfation reaction due to decreased rate of grain growth at lower temperatures. The bottom half of Figure 3 also shows the residence time in the sulfation zone (1500 to 1200 K, 2250 to 1700 F) as a function of the overall residence time. If the sorbent is injected below 1500 K, the effective residence time in the sulfation zone decreases rapidly. In addition, a larger portion of the available residence time must be used for in situ calcination of the stone, and lower temperatures produce reduced diffusion and chemical rates. Therefore, the overall optimum injection temperature appears to be near the front of the sulfation window (approximately 1500 K). Injection above this temperature results in decreased sorbent activity due to excessive grain growth (sintering); injection significantly below 1500 K (2250 F) produces higher initial surface areas but this effect is more than compensated for by the decreased chemical reaction, product layer diffusion rates, and available residence time.

THERMAL HISTORY

Figure 4-a shows the results of detailed heat transfer calculations (made by W. Richter at EER) on the detailed gas temperature profile within the sulfation zone for three full scale utility boilers (solid lines). Time zero was arbitrarily defined to be the point in the boiler where the gas temperature reached 1500 K (2250° F) and the profiles have been characterized in terms of an average quench rate within the sulfation zone (1500 to 1200 K). These results indicate that the quench rate of commercial boilers may vary by as much as a factor of 5 and that in typical utility boilers the time available in the sulfation window may be as little as 1 sec. Figure 4-a also shows measured temperatures (dotted lines) for two thermal profiles produced in the BSF: one, termed the "American Boiler" profile, which represents current field practice; and the other, termed "reduced load," which has a more favorable quench rate.

Figure 4-b summarizes the influence of quench rate on SO_2 capture with downstream sorbent injection at a Ca/S ratio of 2.0. Two very different sorbents were used in these studies: Vicron limestone which represents a typical low surface area calcium carbonate, and Genstar pressure slaked lime which is typical of the high surface area dolomitic hydroxides. The dashed line represents capture predictions generated by EER's grain model. No model parameters were adjusted to improve the agreement between the experimental results and the model predictions; the fundamental diffusion and kinetic rates were based on the data of Borgwardt(6), the surface areas for both sorbents were based on the bench scale measurements of Slaughter et al.(16), and the thermal profile was based on the measured temperatures shown in Figure 4-a. Overall the agreement between the predictions and the data is excellent and, as expected, capture decreased with increasing quench rate because reaction time decreased. These results indicate that a particular sorbent injected under identical conditions in two separate boilers may produce different capture efficiencies because of variations in the thermal characteristics of the boilers.

IMPACT OF FUEL SULFUR

The influence of fuel sulfur concentration was studied by varying the amount of H_2S doped into the natural gas flames. SO_2 concentrations of 500, 1000, 1800, and 3000 ppm (dry, 0% O_2) were tested with Colton lime and Genstar, pressure slaked dolomitic lime (type S). The Ca/S ratio was held constant at 2.0, and the sorbent was injected at 1500 K (2250° F) for all of the runs. These results are presented in Figure 5 along with model predictions. Both the data and the model showed an increase in sulfur capture with increasing SO_2 concentration. The curvature in the theoretical predictions, which is in agreement with the experimental results, is due to a trade-off between the zero order chemistry and the first order pore and product layer diffusion processes. At low SO_2 concentrations the product layer diffusion resistance (which is first order in SO_2) exceeds the chemical reaction resistance (zero order with respect to SO_2) for a larger fraction of the sulfation zone residence time; hence, the overall dependence on gas phase SO_2 concentration is much stronger than at high SO_2 concentrations where the chemical resistance is more limiting. The good agreement between the model predictions and the experimental data is typical of that observed with other sorbents and suggests that the model accurately represents the concentration dependence of the sulfation process.

INFLUENCE OF SORBENT COMPOSITION

Sorbent composition and other physical properties are probably the most important factors in determining overall capture performance. With all other variables held constant, a wide range of sulfur capture can be produced with different sorbent types. This fact is clearly illustrated in Figure 6: capture with downstream sorbent injection ranged from 30% for Vicron to over 75% for pressure slaked dolomitic sorbents at a calcium to sulfur ratio of 2.0. The range in capture with high temperature injection (with the fuel) was not as broad (20 to 40% at Ca/S = 2.0) because the final surface area is less dependent on the initial sorbent characteristics when the calcination occurs at flame zone temperatures(15). In general the capture results tend to be grouped primarily by general sorbent type. On a calcium molar basis, the three pressure slaked dolomitic sorbents gave the best capture with downstream injection. They were followed by the natural dolomite, the two normal slaked limes, and finally the Vicron limestone. For injection with the fuel, both the natural dolomite and the pressure slaked dolomite gave the highest capture while the calcitic carbonate (Vicron) and the calcitic hydroxide gave the lowest capture. (Detailed sorbent characteristics are given in Table 1.)

Since the sorbents shown in the composite comparison include both calcitic and dolomitic materials, the total mass feed rate can very substantially for a given Ca/S molar ratio; hence, both the initial sorbent cost and the amount of ash which must ultimately be disposed of are variable. In order to compare the different sorbents on a total mass output basis, the abscissa in Figure 6 was converted to the mass parameter, MgO + CaO divided by the total inherent coal ash (assuming a 1% sulfur and a 10% ash coal) as shown in Figure 7. Compiling the data on this basis gives an indication of the capture that can be achieved relative to the amount of additional material that passes through the convective passes and that must be removed from the particulate collection devices. Even on this basis the dolomitic pressure slaked limes appear attactive as does the Warner slaked lime. Again the poorest performance was achieved with the Vicron limestone. These results suggest that capture in excess of 60% can be achieved with approximately a 50% increase in the dry ash handling requirements for a 1% sulfur coal or a 150% increase in solids loading for a 3% sulfur coal.

Since the results shown in both Figures 6 and 7 indicate that dolomitic sorbents are effective in achieving sulfur capture, the role of magnesium was of particular interest. Figure 8-a shows the influence of magnesium content for several slaked sorbents at different quench rates. As noted previously the overall capture is significantly higher for the thermal conditions with the reduced quench rate (longer sulfation zone residence time). Capture also increased significantly as the magnesium content increased. The role of magnesium was examined directly by injecting $MgCO_3$ alone and in a mixture with the Vicron limestone to achieve a "simulated dolomite." The Ca/Mg molar ratio of the mixture was kept the same as the real dolomite, and the results from these tests are shown in Figure 8-b. The data from the downstream injection of $MgCO_3$ alone suggest that it does not significantly react with SO_2 to form magnesium sulfate prior to the sampling point (1200 K) and this consistent with both theoretical considerations and previous practical experience. The simulated dolomite gave essentially identical capture to that measured previously for the Vicron limestone alone, again confirming that $MgSO_4$ formation was not significant. Apparently, the magnesium in the dolomitic materials enhances the capture by means other than direct capture since mere physical mixing of the two materials does not yield the high capture produced with dolomite where the magnesium is present as an integral part of the sorbent matrix. It has been previously suggested that the magnesium prevents pore blockage, but the characteristic particle size in the Genstar pressure slaked dolomite is less than 1 µm and with sorbent particles that small, the pore diffusion resistance is insignificant. A more likely explanation appears to be that the Mg enhances product layer diffusion and/or initial chemisorption of the sulfur species.

SORBENT ENHANCEMENT BY PROMOTER ADDITION

One of the primary aras of study in the BSF has been the addition of various promoters to enhance sulfur capture. Initially, Cr_2O_3 was found to dramatically improve capture with Vicron, especially when the promoted sorbent was injected into the high temperature region at the burner. Many of the transition metal promoters were evaluated for possible capture enhancement; however, only molybdenum and chromium enhanced capture significantly, relative to Vicron. Subsequently, Borgwardt found that alkali metal compounds (lithium, sodium, potassium) gave positive results similar to those found with the chromium series materials. Figure 9 shows that mixing each of the alkali metal carbonates with Vicron resulted in increased SO_2 capture when the sorbent was injected with the fuel and downstream. In these experiments the ratio of metal ion to calcium was maintained equal to that for the 5% Cr_2O_3 addition. On this basis chromium proved to be the best promoter in terms of overall capture. The most unusual thing about the chromium promoted limestone sorbent was that, in contrast to all previous results, the capture with high temperature injection was equilavent to that with downstream, low temperature injection. Chromium appears to have the ability to counterbalance the effect of thermal sintering of the sorbent. Figure 10 illustrates the influence of Cr_2O_3 addition with other types of sorbents. The open bars represent the capture measured with the sorbents alone, and the shaded bars indicate the increase in capture that resulted from 5% chromium addition. With all of the sorbents and with both burner zone and downstream sorbent injection, the capture increases with chromium promotion were significant. Even the performance of the Genstar pressure slaked dolomite was improved: 70 to 85% capture for the downstream sorbent injection and 35 to 70% capture for injection with the fuel. In general the enhancement above the base line was greater when the promoted sorbents were injected into the high temperature region, although the absolute capture levels were generally higher for downstream injection.

The exact mechanism for the chromium and sodium enhancement is not clear at the present time; however, it appears likely that these materials promote capture by enhancing the product layer diffusion step since the model calculations indicate that product layer diffusion is the primary limitation to increased sulfation rates. Additional work is needed to optimize the method of promoter addition and clarify the controlling mechanisms.

CONCLUSIONS

The experimental results and the sulfation model calculations indicate that the sorbent injection locations and the residence time within the sulfation temperature window can significantly influence the overall sulfur capture for any particular sorbent. Unless the sorbent is promoted with a metal additive, downstream injection at approximately 1500 K (2250° F) results in optimum sorbent utilization. Increasing the heat removal rate between approximately 1500 K and 1200 K (2250° to 1700° F) results in decreased sulfur capture. Increasing the gas phase SO_2 concentration (e.g., due to increased coal sulfur content) improves sorbent utilization, but the dependence is non-linear due to the combined effects of intrinsic chemistry and diffusion.

In general dolomitic sorbents perform better than calcitic sorbents (per mole of Ca) and hydroxides are superior to carbonates. The true influence of pressure slaking is unclear; however, the best sorbents tested (on either a calcium molar basis or total mass basis) were the pressure slaked dolomites. The magnesium in the dolomite materials does not react to produce magnesium sulfate; it probably enhances product layer diffusion. The performance of all sorbents can be enhanced by the addition of appropriate metallic compounds in relatively small quantities.

Thus, the results of this study suggest that it is possible to achieve capture levels significantly above those typical of limestone injection by at least two alternative methods: use of specially treated sorbents (e.g., pressure slaked dolomites) or use of promoted limestones. (Clearly these two concepts can be combined to produce even higher capture levels; however, this may be economically unattractive.) Figure 11 provides an overall comparison of these alternatives under conditions that were designed to approximately simulate current utility practice (American Boiler profile). In general these data show that, even under severe thermal conditions (quench rate = 330 K/sec = 600° F/sec), it is possible to achieve 40% capture with approximately a 70% increase in boiler solids loading (based on a 10% ash, 1% S coal) by injecting either an inexpensive limestone promoted with a metal oxide or a pressure slaked dolomite.

ACKNOWLEDGMENTS

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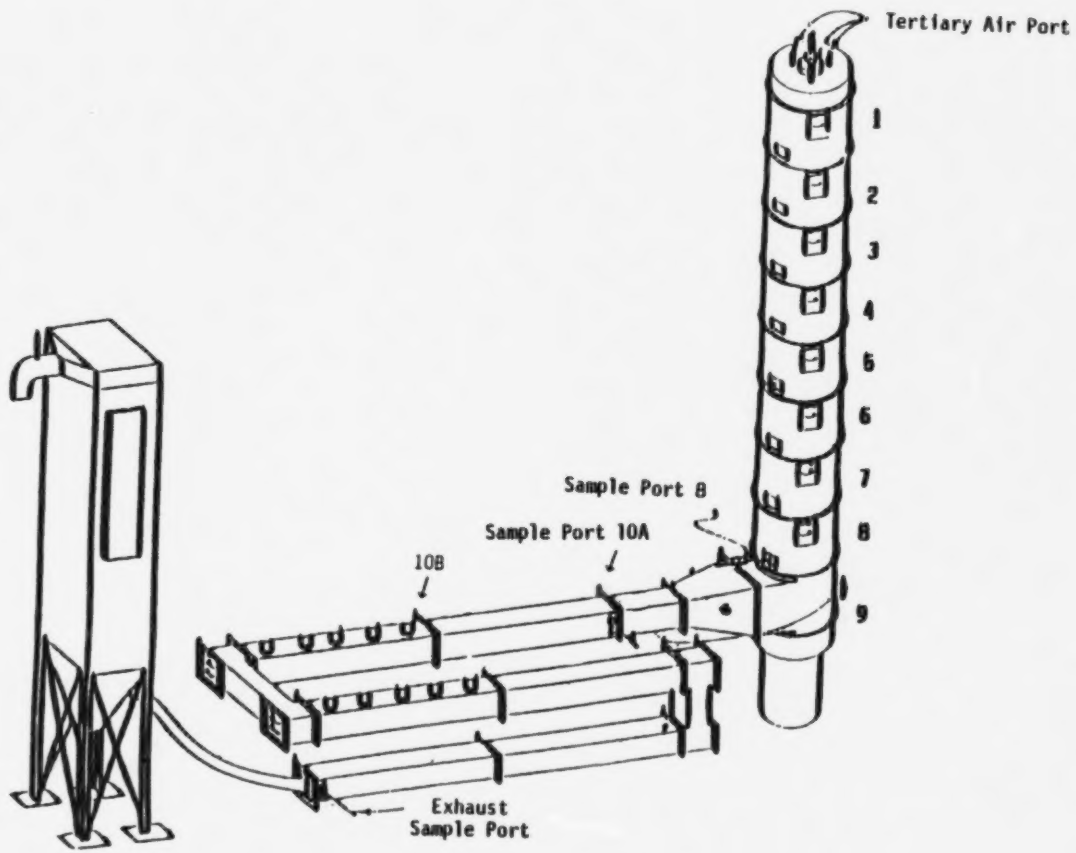
Tertiary Air Port
1
2
3
4
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8
9
Sample Port 8
Sample Port 10A
10B
Exhaust
Sample Port

Figure 1. Boiler simulator furnace.

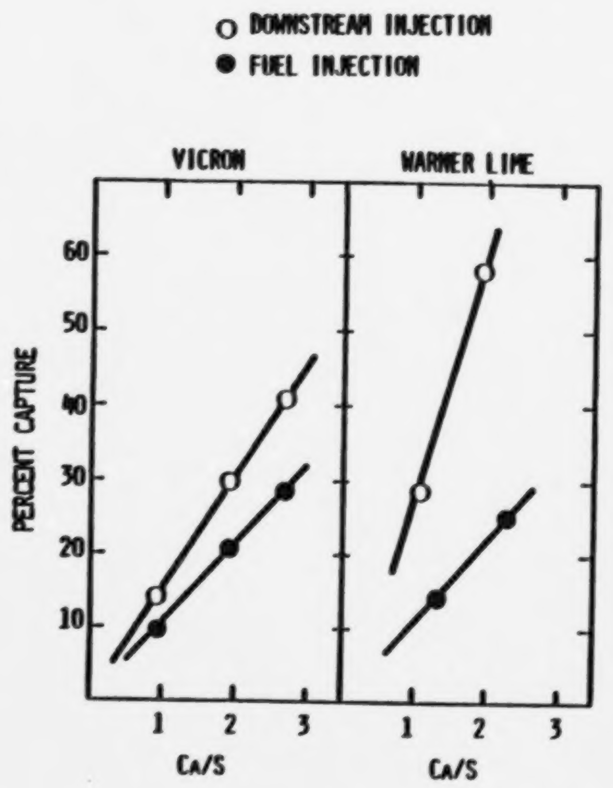


Figure 2. Influence of injection location on sulfur capture.

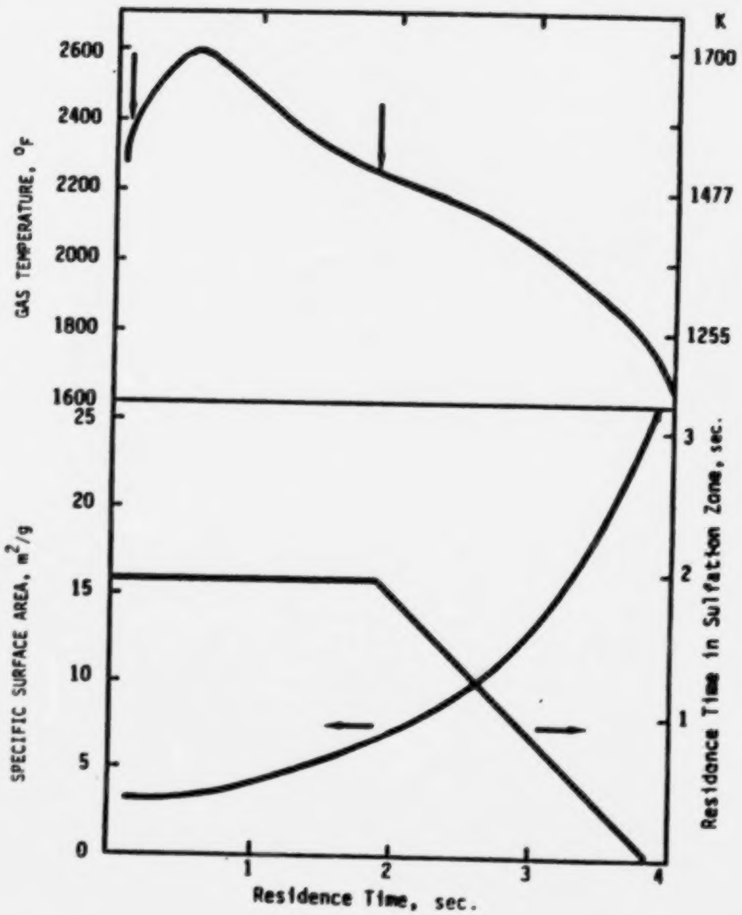


Figure 3. Impact of injection location on residence time and surface area.

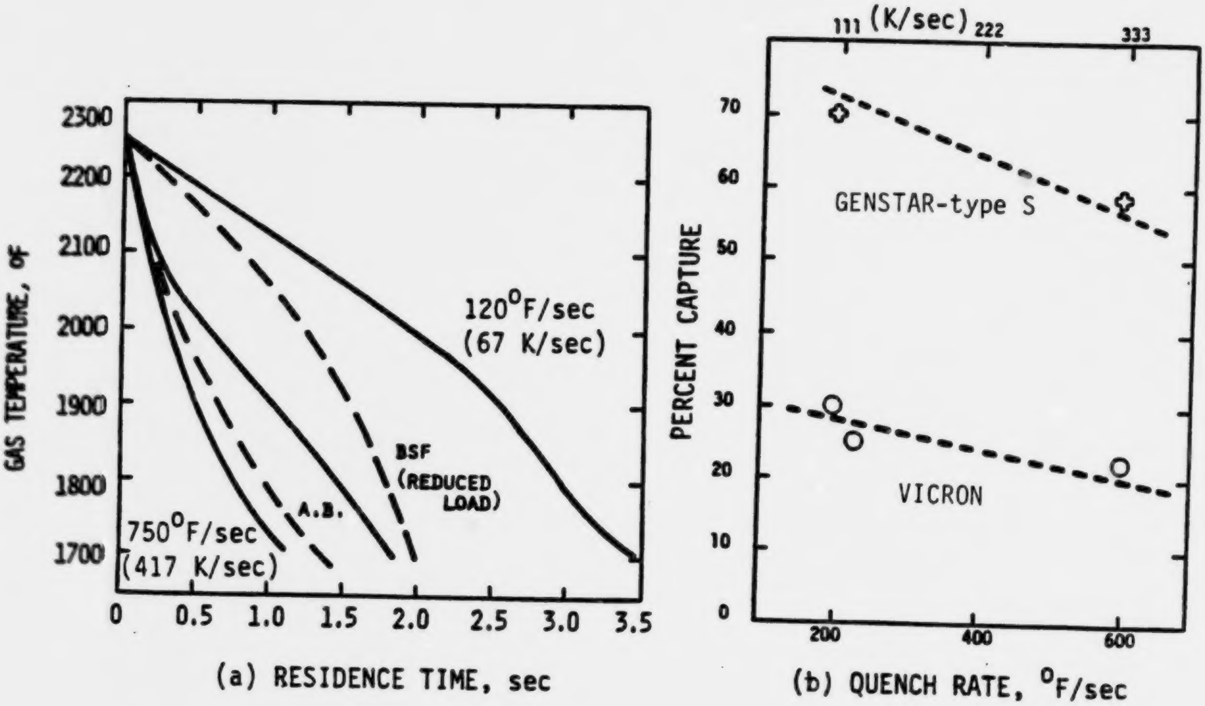


Figure 4. The effect of quench rate in sulfation zone.

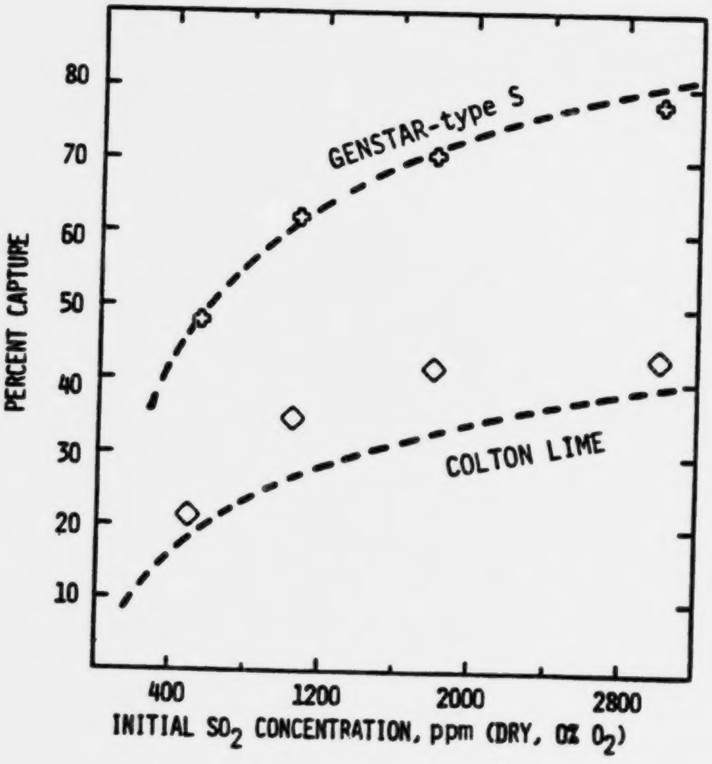


Figure 5. The effect of initial SO_2 concentrations.

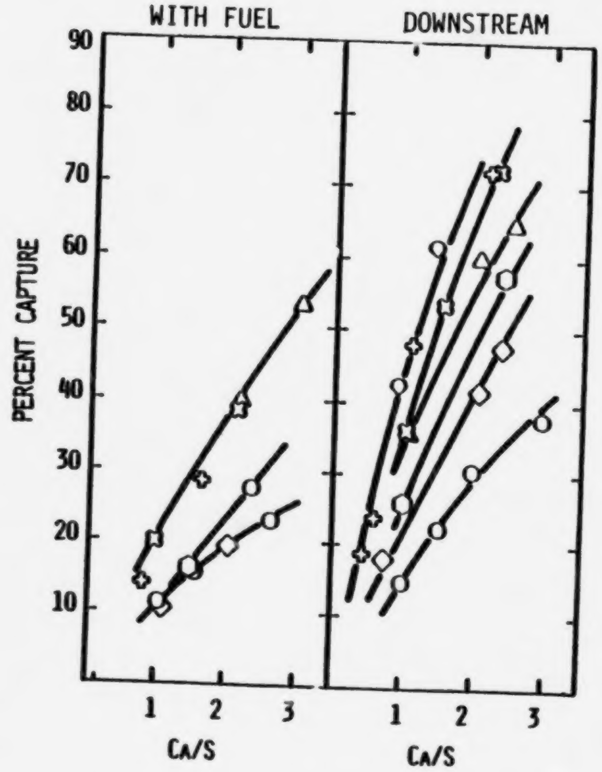


Figure 6. Capture comparison (reduced load, natural gas/H_2S; see Table 1 for symbol key).

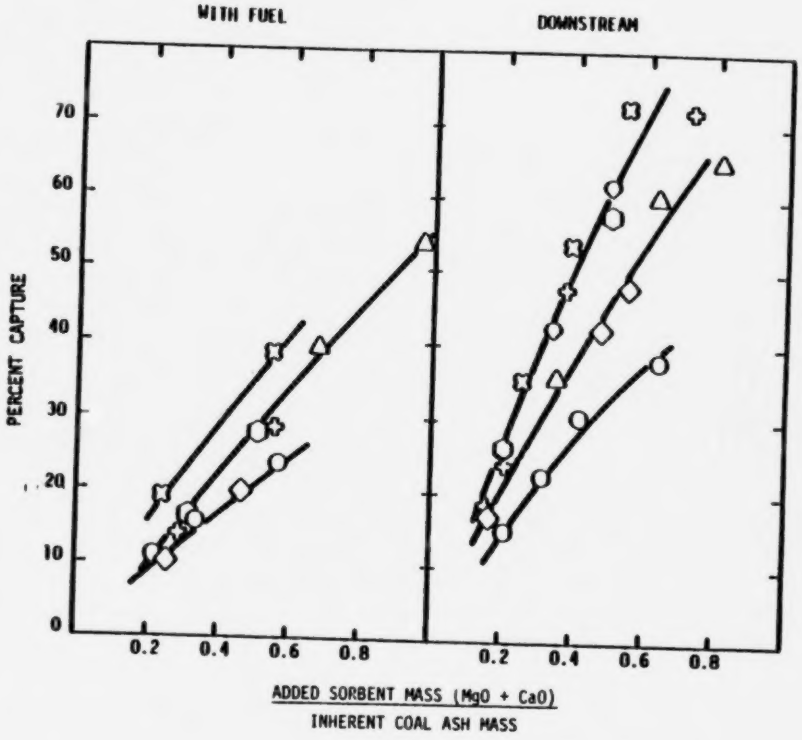
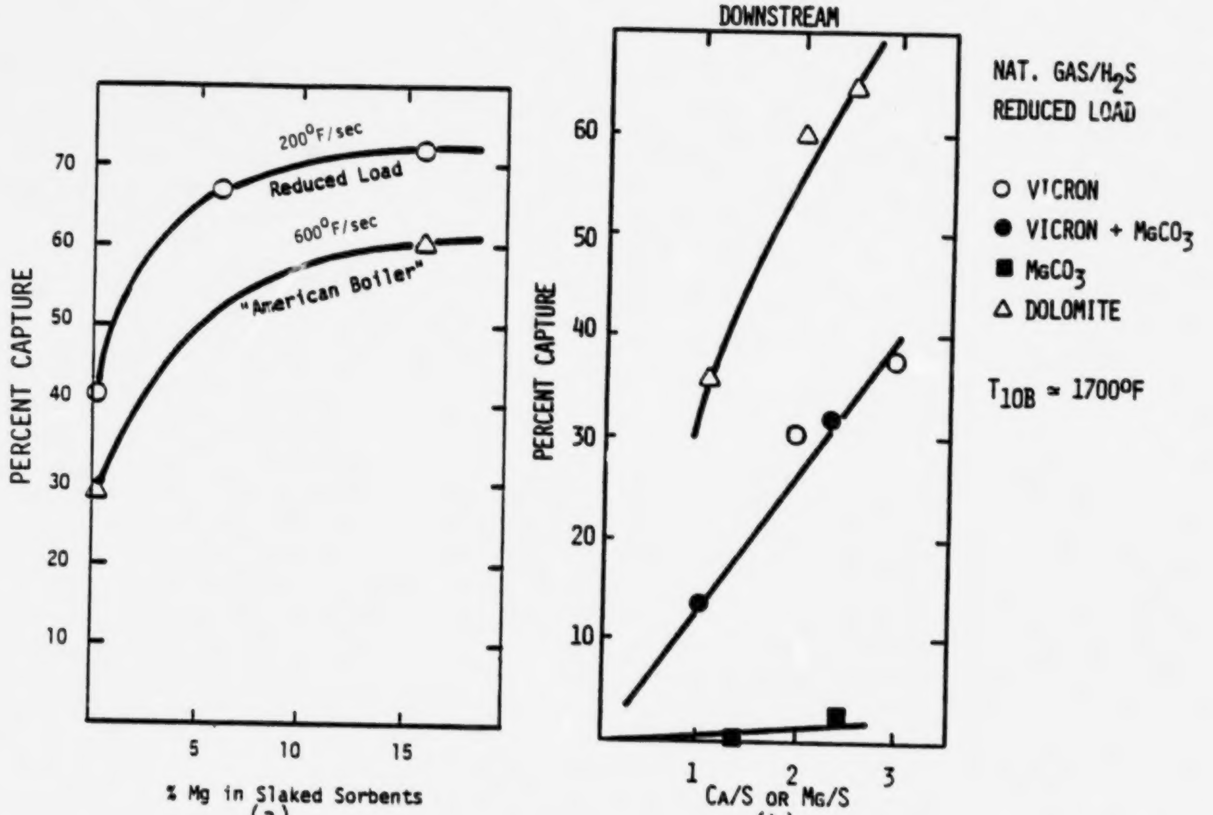


Figure 7. Capture comparison - mass basis (10% ash, 1% S coal).



(a) (b)

Figure 8. Influence of magnesium.

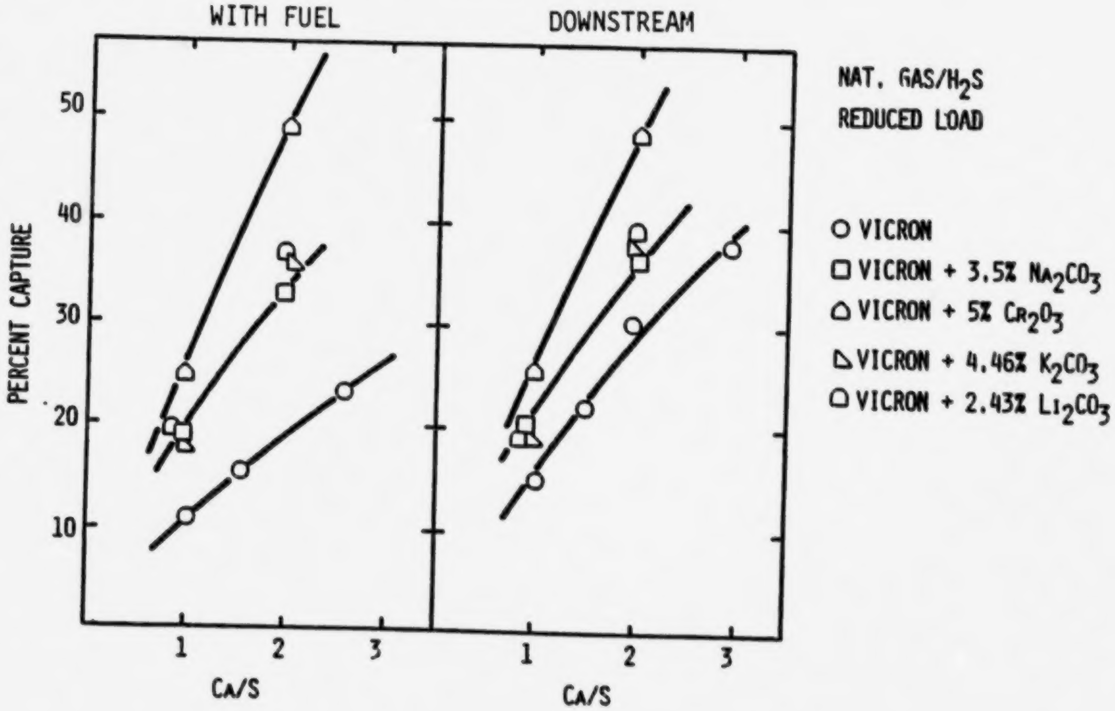


Figure 9. Additive screening results.

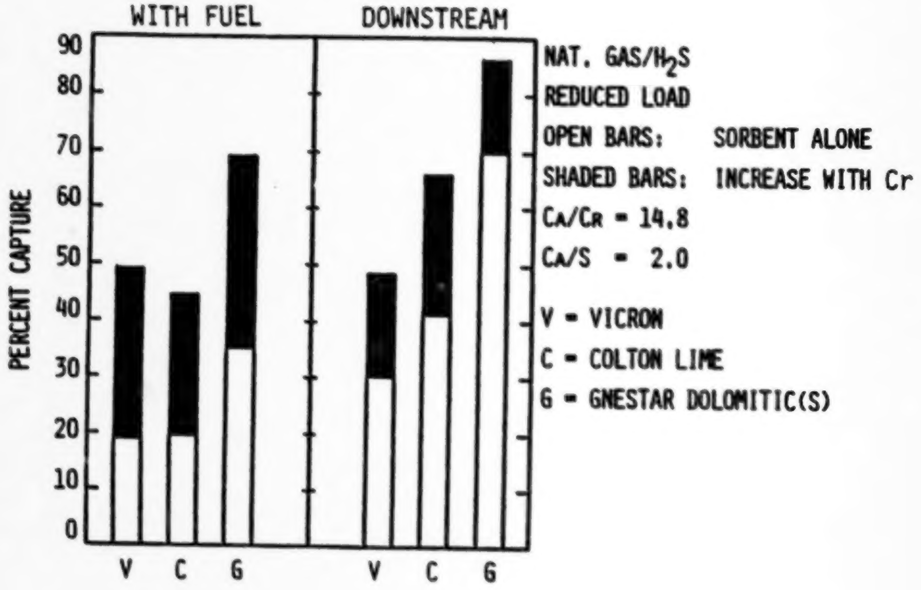


Figure 10. Capture enhancement with Cr_2O_3.

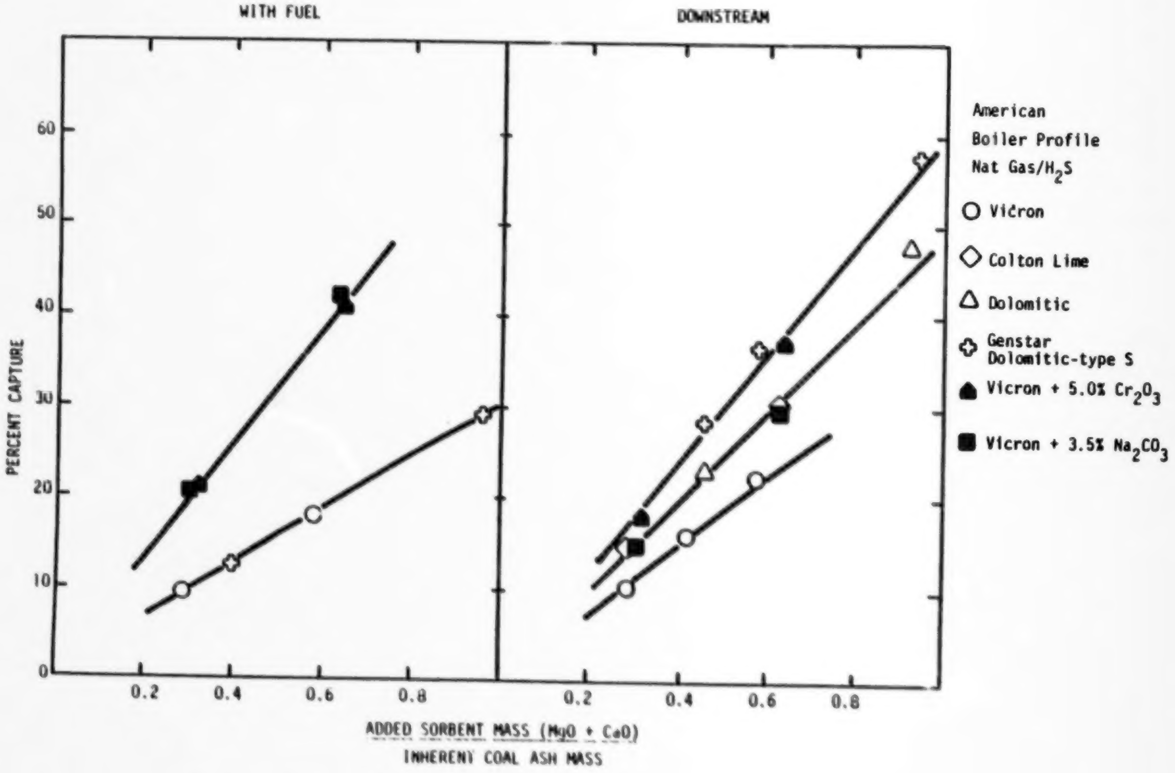


Figure 11. Overall comparison.

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF SORBENTS

Sorbent	○ Vicron	◇ Colton Lime	⬡ Warner Lime	△ Dolomite	✕ Genstar Blend (S)	✚ Genstar Dolomitic (S)	⬠ Warner Dolomitic (S)
Type	Calcite	Hydrated Lime	Hydrated Lime	Dolomite	Hydrated Lime + Hydrated Dolomitic Lime	Pressure Slaked Dolomitic Lime	Pressure Slaked Dolomitic Lime
Composition	$CaCO_3$	$Ca(OH)_2$	$Ca(OH)_2$	$CaCO_3 \cdot MgCO_3$	$Ca(OH)_2 + Ca(OH)_2 \cdot Mg(OH)_2$	$Ca(OH)_2 \cdot Mg(OH)_2$	$Ca(OH)_2 \cdot Mg(OH)_2$
Mean Size (μm)	9.8	4.0		11.8	1.8	1.4	3.5
Density (g/cm^3)	2.7	2.3		2.9	2.3	2.3	2.3
Chemical Comp (%)							
Ca	39.2	51.4	53.9	24.8	45.0	30.3	29.5
Al	0.02	0.21	0.37	0.04		0.26	0.21
Si	0.09	3.30	0.51	0.16		0.13	0.94
Fe	0.06	0.10	0.21	0.09		0.07	0.42
Na	0.007	0.007		0.007			
Mg	0.33	0.25	0.20	11.3	6.2	16.0	15.9

STUDIES OF SORBENT CALCINATION AND SO_2-SORBENT REACTIONS IN A PILOT-SCALE FURNACE

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ABSTRACT

Furnace injection of calcium-based sorbents for SO_2 reduction was examined using a 1×10^6 Btu/hr pulverized coal-fired combustor. The effects of sorbent type and rate, residence time, injection site, staged combustion, and CO_2-enriched transport air on overall SO_2 removal are reported. Properties of calcine were determined for gas firing at selected conditions. Variations in calcine surface area of 2 to 30 m^2/g were found, corresponding to a range of calcium utilization of 12 to 38%. Sorbent type and temperature at the point of injection were primary determinants of calcium utilization.

STUDIES OF SORBENT CALCINATION AND SO_2-SORBENT REACTIONS IN A PILOT-SCALE FURNACE

INTRODUCTION

The Electric Power Research Institute (EPRI) and Southern Company Services (SCS) are co-funding a project with the objective of developing a dry sorbent emission control process (DSEC) as a means of reducing sulfur dioxide emissions from coal-fired boilers. The program consists of an ongoing technology assessment, fundamental bench-scale studies, small pilot-scale studies, and a conceptual design study for a 40- to 80-MW scale application of DSEC. This paper presents results obtained using a 1×10^6 Btu/hr combustion system at Southern Research Institute.

A major task in the overall process development effort consists of obtaining an understanding of the mechanisms which limit sorbent utilization under various conditions. Accordingly, the pilot-scale experiments have been supported by an extensive analytical effort to provide detailed chemical and physical characterization of fuels, raw and reacted sorbents, and calcines. The objectives of the pilot-scale study may be described more specifically as follows:

- Provide a means of evaluating sorbents and process modes under realistic conditions
- Define the sorbent properties and process conditions which limit SO_2 capture and calcine utilization
- Develop a data base for calcium utilization as a function of sorbent type, firing conditions, fuel, injection mode, and calcine properties
- Evaluate an integrated process which combines furnace injection with downstream injection

The results obtained to date in the pilot-scale program are primarily concerned with determinations of calcine properties and calcium utilizations with furnace injection of high calcium sorbents.

TESTING PROCEDURES AND EQUIPMENT

Combustor

An overall view of the pilot combustor system is shown in Figure 1. The furnace is a down-fired, refractory-lined cylinder with a nominal capacity of 1×10^6 Btu/hr. Dimensions of the furnace and location of sampling and sorbent injection ports are shown in Figure 2. The furnace is equipped with an adjustable-swirl burner, and with injection or sampling ports as shown. The baseline firing conditions are given in Table 1. Figures 3 and 4 show radial temperature profiles for the baseline firing conditions with 1.0 and 0.6×10^6 Btu/hr fuel rates.

Note that firing with gas gives much higher temperatures near the burner than does coal. The difference is especially pronounced with the lower firing rate. Temperatures with either fuel are similar downstream from the burner (not shown).

The combustion gases leaving the furnace pass through a horizontal, refractory-lined tunnel ("square duct") and then through air-cooled stainless steel piping. The gas cools to 150 to 300°F before entering a pulse-jet baghouse.

Coal and sorbent are fed gravimetrically into separate eductors and transported to the furnace. Sorbent, when injected at the burner, passes through the burner core with the fuel entering a surrounding annulus. Sorbent is injected downstream of the burner through two opposed 1/2 in. jets perpendicular to the furnace axis.

Residence Time Considerations

Temperature-time profiles showing port locations are given in Figure 5 for baseline firing conditions. The change in slope after Port S-5 corresponds to the furnace exit. The 1×10^6 Btu/hr profile is compared in Figure 6 to residence time-temperature values for four utility boilers. Values for Units 1, 2, and 3 were calculated from firing rates and temperatures reported for t-fired 300 to 600-MW boilers operated near rated capacity (1).

It is emphasized that the calculated values are based solely on average flue gas velocity and average gas temperatures at several elevations within the radiant section. The values for Unit 4 are those reported for a 140-MW, wall-fired unit (2), and show a much steeper gradient. The lowest temperature for each of the four units corresponds to the radiant section outlet; the temperature would be expected to drop much faster on entering the convective passes. The 1×10^6 Btu/hr temperature profile of the pilot unit radiant section is a reasonable approximation of that in certain full-scale units, and probably provides more time in the 2000 to 2200°F region than most boilers at rated load. (Reduced load data for Units 1, 2, and 3 were not available.) The pilot unit fired at 0.6×10^6 Btu/hr provides much more time in the 2000°F region than would be expected in a full-scale boiler.

Continuous Gas Analysis

A sample is withdrawn through an in-stack sintered stainless steel filter at a point where the gas temperature ranges from 250 to 500°F (depending on firing rate). The filtered sample passes through a conditioner which removes water by condensation at 35 to 40°F. Equilibrium calculations show that, in the absence of alkaline contaminants, the maximum loss of SO_2 to the condensate from coal or natural gas combustion would be 1.5 and 3%, respectively. Condensate collected during coal combustion with injection of hydrated lime contained negligible calcium and the equivalent of 1% of the gas phase SO_2. The suitability of this sample system has also been demonstrated by injecting SO_2 into the flue gas just ahead of the sample probe. During natural gas firing, the recovery of SO_2 in the absence of sorbent is typically 97 to 99% of the value calculated from the measured feed rates of SO_2 and fuel. Initiation of furnace sorbent injection results in a reduction of SO_2 from 4 to 14% of that which occurs when the SO_2 is added with the fuel. That is, of the loss in SO_2 measured when sorbent reacts with SO_2 throughout the combustor system, only 4 to 14% occurs in the sampler itself. This is an especially severe test of sample system bias in that the SO_2 injected at low temperature is exposed to unsulfated sorbent. The results must be viewed as an upper limit in sample system bias since some of the reaction may occur between injection and sampling rather than in the sample system itself. A less severe test, in which SO_2 was injected near the sampler during coal firing, showed no difference in the recovery of added SO_2 with or without sorbent injected. Tables 2 and 3 list the results of these tests.

Fuel and Sorbents

All tests with coal to date have been made with a Jefferson seam, Alabama coal produced by the Hallmark mine. Coal and ash analyses typical of Lot 1 are shown in Table 4. Recent tests have been made with a second lot of the same coal which differs from the first only in sulfur content (2.8 versus 3.4% for the first lot). The coal is pulverized on site to about 80% minus 200 mesh.

Extensive pilot-scale testing has been completed with two varieties of limestone, a high-calcium hydrate and a pressure-hydrated dolomitic lime. Table 5 lists complete analyses for these materials. The St. Genevieve limestone is a relatively pure carbonate with fine, uniform grains, and with a correspondingly low surface area of 1.5 m^2/g. The Marianna limestone, in contrast, features irregular grains, some fossil remains, sigificantly more impurities, and higher surface area. Both hydrate materials exhibit characteristically smaller size distributions and higher surface areas.

Limited testing has been completed with the following sorbents: three additional grades of the St. Genevieve limestone ranging from 1.5 to 15 μm MMD; four additional grades of Marianna limestone ranging from 1.3 to 35 μm MMD; two grades of pulverized marble; two precipitated calcium carbonates having mean diameters of 0.7 and 0.07 μm; a dolomitic limestone; and a high-calcium, pressure-hydrated lime. Some properties of these materials are listed in Tables 6 and 7.

Description of Test Procedures

This section describes the two types of tests carried out with the pilot-scale combustor: those in which only the gas-phase reduction of SO_2 with the introduction of sorbent during coal-firing was determined; and those in which solids samples were collected during gas firing for further characterization.

Reduction of gas-phase SO_2. The standardized test chosen to evaluate a large number of variables on the basis of overall SO_2 removal was the following: 1) establish steady state at the conditions of interest; 2) begin feeding sorbent to the sorbent eductor; 3) terminate sorbent addition after 10 min. Table 8 gives the definitions used for reporting calcium-to-sulfur ratio, SO_2 reduction, and calcium utilization.

The gas sampling system has been shown to make no contribution to the reduction of SO_2. That the contribution of deposited sorbent to the overall reduction is minor is inferred qualitatively from the similar response of the system either to sorbent initiation or to reduction in SO_2 feed. Analysis of solid samples has in general confirmed the apparent utilization calculated from gas composition.

Solids sampling. Solids samples were withdrawn from the furnace through a water-cooled probe and collected in a glass-fiber thimble at the probe exit. The central sample tube is separated from the coolant by an annulus through which diluent may be added to the sample at the probe entrance. Initial experiments showed that in-probe reaction of calcine sampled either with or without dilution resulted in no more than 1 to 2% each of H_2O, CO_2, or SO_x in the solid. Thus, the sampling procedure adopted for this study was to sample undiluted flue gas while maintaining the cooling water exit temperature at 130°F and the collecting filter at 300°F to avoid condensation.

Subsequent to these initial probe validation tests, much more reactive calcines were encountered. Injection of high-calcium or dolomitic hydrated lime in the lower furnace, for example, yields calcines with surface areas of 10 to 15 or 30 to 40 m^2/g (compared to 2 to 3 m^2/g for the calcine from burner injection of limestones in the tests cited above). With these calcines, $Ca(OH)_2$ and $CaCO_3$ each account for

5 to 20 mol % of the total calcium. The reactions to hydroxide and carbonate are assumed to occur in the probe since the temperature in the furnace is well above the decomposition temperature of either.

Figure 7 shows the potential for in-probe reaction of SO_2 with the most reactive calcine tested. In these tests, calcine was sampled during injection of dolomitic hydroxide at S-4. One series was completed with SO_2 added to the gas flame (normal sampling). A second series was then completed with no SO_2 added to the flame, but with SO_2 added to the inlet of the probe. Any sulfate present in the second series of samples had to be due to reaction within the probe itself. At the level of injection, the in-probe reaction is equivalent to the overall reaction when SO_2 is present in the furnace (normal sampling). Clearly, this sampling procedure gives no information on the extent of in-furnace sulfation at the level of injection. Although it appears that in-probe reaction could account for as much as 30% of the utilization measured at S-5 and SD-2, such is not likely the case. When SO_2 is present only in the probe, the reaction is with "fresh" calcine, and represents only an upper limit in additional in-probe reaction of sulfated calcine. The agreement between solids analysis and exit SO_2 reduction (measured at about 700°F, as described previously) supports the idea that additional reaction in the probe is much less.

Neither elevation of the filter temperature to 500°F nor use of air rather than water as a probe coolant appeared to make a consistent difference in calcine BET area or composition. While work continues on the development of a better sampling technique, the present results are thought to be deficient only for the most reactive calcines.

EXPERIMENTAL RESULTS

Results of Screening Studies

This section discusses the results of tests wherein only the overall reduction in SO_2 was measured. Variables examined include: sorbent type, sorbent rate, fuel rate, injection site, staging of combustion air, and CO_2 addition to the sorbent transport air.

Sorbent type and rate. Figure 8 compares the performance of four basic types of sorbents: limestone, dolomite, calcium hydroxide, and dolomitic hydroxide. The SO_2 removals shown are the optimum for each sorbent with 1×10^6 Btu/hr firing. The results shown for Marianna limestone are very similar to those for St. Genevieve under these conditions. The removals achieved with the pressure-hydrated, high-calcium lime were the same as with the Longview $Ca(OH)_2$.

Better utilizations have been achieved with injection of Marianna limestone at lower temperatures and with extremely fine grades of calcium carbonates. The results of Figure 8, however, are representative for each class of sorbent. The enhanced calcium utilization of the dolomitic sorbents is offset by the lower calcium content. Figure 9 shows the same removal data plotted as a function of the mass feed rate of sorbent. The collapse of the data for four sorbent types into two distinct lines is fortuitous, but does illustrate the improved performance of hydrates and the weight-basis penalty resulting from the presence of the inert magnesium. (Analysis of sulfated dolomitic samples showed that sulfation of magnesium was negligible.)

Injection site and residence time. The gas temperature at the level of sorbent injection was the most important variable in determining the utilization of a given sorbent. Figure 10 shows that the removals achieved with Marianna limestone injected with different firing rates and fuels lie along a single curve. Note, for example, that the removal was similar for injection either at S-2 with low-load gas firing, or at S-4 with high-load coal firing. The temperatures at the level of injection are similar for these two cases, whereas the time-temperature profiles are markedly different.

Additional combinations of injection temperature and residence time were tested with the following experiment. SO_2 removal was determined for S-3 injection of Marianna with natural gas firing rates ranging from 0.55 to 1.0 x 10^6 Btu/hr. The combustion air, SO_2 feed, sorbent, and sorbent transport air, however, were held constant at the rates appropriate for 1.0 x 10^6 Btu/hr. The temperature at the injection level was thus varied from 1500 to 2350°F while maintaining constant geometry and mixing. Wet flue gas volume and hence, in situ sorbent and SO_2 concentrations, changed less than 5% over this range. Gas composition effects other than SO_2 are assumed to be of secondary importance. Figure 11 shows that the temperature dependence was nearly identical with that shown in Figure 10, where injection site, flue gas rate, and fuel type were variables. The temperature dependence differed only when sorbent was injected at the furnace exit with the load increased to 1.2 x 10^6 Btu/hr; that is, the region where the temperature decay is very rapid. For injection at temperatures from 1730 to 2000°F, SO_2 removal was 14 to 38% under these conditions of rapid temperature decay.

For all the tests cited above average residence times were calculated for discrete temperature regions. Figure 12 shows calcium utilization plotted as a function of available reaction time between 1600 and 2200°F. This is a rather crude analysis which assumes that no $CaSO_4$ can be formed above 2200°F, and the reaction rate is negligible below 1600°F due to chemical kinetics. This plot is presumably consistent with a diffusion-controlled process that produces a negligible increase in sorbent utilization in a reaction time exceeding two seconds, regardless of temperature within the stipulated range.

From Figures 10, 11, and 12 it is clear that injection temperature (i.e., calcination/sintering) determines the upper limit for utilization of this sorbent on pc-fired boiler time scales. Figure 12 should, in principle, be plotted as a utilization-versus-residence time curve for each injection temperature (or calcine surface area, or some other measure of reactivity) but this is not warranted by the limited number of data points and uncertainties in time-temperature characterization of the pilot combustor. The time scale in Figure 12 should be viewed as relative, rather than absolute, but does demonstrate that most of the potential utilization is achieved rather quickly.

The utilization of St. Genevieve limestone is very similar to that of Marianna over the 2200 to 2700°F range of injection temperatures. It does not, however, exhibit the marked increase in performance shown by the Marianna in the 1800 to 2200°F range.

The performance of high-calcium and dolomitic hydroxides over a range of temperatures is shown in Figures 13 and 14. Both show a peak in SO_2 removal with injection between 2000 and 2200°F. A detailed analysis of the relative importance of residence time has not been made for these sorbents.

Particle size effects. Two grades of St. Genevieve and Marianna limestone were initially tested to examine particle size effects over a range realistic for full-scale pulverizer capabilities. The grades thus referred to as coarse and fine correspond to an MMD of 15 and 7 μm for the St. Genevieve, and 35 and 13 μm for the Marianna limestone. The size range was extended by air jet milling the fine grade of each to achieve a product MMD as small as 1.3 μm. Precipitated calcium carbonate products having mean diameters of 0.7 and 0.07 μm were also tested. Figure 15 shows the utilization of each sorbent as a function of mean particle size for either burner or S-4 injection, with baseline firing conditions at 1 x 10^6 Btu/hr. Utilizations of 25 to 30%, comparable to that of hydrated lime, are observed for the finest pulverized carbonates and the precipitates injected at S-4 (~2200°F). Very little increase in utilization with decreasing size is seen for burner injection. It was expected that since more of the surface area of the very fine particles can be accounted for by external rather than pore area, these sorbents would be less sensitive to temperature effects. The results indicate, however, that primary particles within agglomerates may be sintering to yield a less reactive calcine before sulfation occurs (i.e., before the temperature decreases below 2200°F). The Multifex, for example, is extremely difficult to disperse, as evidenced by the apparent sedimentation diameter (see Table 7).

The correlations shown in Figure 15 are least-square fits to the data, with MMD considered the only variable. Although no account is taken of other sorbent properties, these correlations may be useful in a cost benefit analysis of various degrees of size reduction.

CO_2 added to transport air. Significant levels of CO_2 in the sorbent jet entering the furnace, as would be found if recirculated flue gas were used for transport, could affect the calcination of carbonate material. Flue gas recirculation was simulated by adding CO_2 to the STA (sorbent transport air) to bring the composition of the transport gas up to 10 to 20% CO_2 (by volume, sampled from the transport line after the sorbent aspirator). When CO_2 was added, the amount of air supplied was reduced to keep the total volume of transport gas constant. For either S-3 or S-4 injection of St. Genevieve limestone, the presence of up to 20% CO_2 in the transport gas had an insignificant effect on the capture of SO_2. The temperature may be high enough (at S-4, typically 2200°F) that calcination is little affected by the presence of CO_2. In addition, if particle heating is predominantly due to the entrainment of hot flue gas in the transport air (rather than radiation), the gas surrounding the particles must contain significant CO_2 from flue gas by the time calcination could occur. Hence, the additional CO_2 brought in with the sorbent would not affect calcination.

Staged combustion. Tests with staged combustion were limited to St. Genevieve limestone, added during combustion of coal at 1 x 10^6 Btu/hr. Two basic configurations were examined: sorbent added at the burner so that, with staging, it sees a fuel-rich environment; and sorbent added at the staging level.

Only in the case where the burner stoichiometry was quite low, and the staging air far from the burner, did staging at all improve the utilization of limestone injected at the burner. Less severe staging (in geometry and stoichiometry) resulted in capture equivalent to or lower than no staging.

When sorbent and staging air were both added near the burner, capture was lower than for unstaged burner injection. Removal with S-3 injection of limestone was improved slightly by the addition of staging air at the same location, but only when the staging was fairly extreme (an increase in utilization from 19-20% to 22% with a reduction of burner stoichiometry to 70%). The small improvement in sorbent efficiency is attributed to temperature effects and enhanced mixing by the staging air.

Further work with staging was not warranted by the results of these exploratory tests.

Characterization of Solids Samples

All solids samples were taken during firing with natural gas. As a general rule, no significant differences have been observed in sorbent performance with coal or gas other than those attributable to temperature at the injection point. Properties of the calcine are therefore expected to correspond to sorbent performance with coal. One notable exception is that sorbent injected through the burner is exposed to considerably higher temperatures with gas than with coal, the difference being much more pronounced with low-load firing.

Solids properties reported are BET surface area (by single-point N_2 absorption) and chemical composition. Composition is based on analysis for C, H, and SO_4^{-2} and reported as $CaCO_3$, $Ca(OH)_2$ and $CaSO_4$. For dolomitic samples, all C, H, and S were assigned to calcium. Selected samples have been analyzed more extensively with a wide variety of techniques, but are not discussed in this paper.

St. Genevieve Limestone. Properties of calcine collected during injection of St. Genevieve limestone either through the burner or at S-4 are shown in Figures 16 and 17. Material sampled less than a foot from the burner, directly below the sorbent injector, is nearly 30% calcined. Calcination is complete by S-2. In the case of S-4 injection, material sampled in the plane of injection is 40% calcined, and calcination is complete by S-5. Thus, even with injection at 2200°F, calcination is very rapid. The surface area is at a maximum for the partially calcined sorbent in either case. Calcium sulfate cannot form above about 2200°F, by which point ($T \sim 2200°F$ at S-4) the surface area for the burner injection case has dropped to 2 m^2/g. The BET area in the reactive zone with S-4 injection is at least 6 m^2/g. The surface area of calcine from S-3 injection at 0.6×10^6 Btu/hr was higher at the plane of injection, about 13 m^2/g, but dropped to 8 to 6 m^2/g at S-4 and S-5 (not shown). Calcination was as rapid and as complete as for the cases shown.

Marianna Limestone. Calcine surface areas resulting from three injection modes are shown in Figure 18. Burner injection again yields a very low-area calcine, but at lower injection temperatures the area is increased by up to a factor of 7. More properties of the calcine from S-3 injection at 0.6×10^6 Btu/hr are shown in Figure 19. Figure 20 shows the properties of calcine from an analogous test with SO_2 present. Note the large reduction in surface area apparently due to the formation of sulfate. The implications of significant amounts of hydroxide and carbonate were discussed previously under sampling procedures. The St. Genevieve results suggest that calcination is rapid even at relatively low furnace temperatures. There is no reason to expect the Marianna limestone or hydroxides (discussed below) to calcine less completely. Therefore, the presence of uncalcined material is likely to be due to more extensive in-probe reaction with these more reactive sorbents.

Longview $Ca(OH)_2$. Figure 21 shows that the surface area of calcine from burner injection of $Ca(OH)_2$ is less than 4 m^2/g at the point where sulfation can begin. With injection at a very low temperature, about 1800°F, the calcine area is increased to 12 m^2/g. Sulfation of a calcine from a similar test lowered the area by about 30%. With S-4 injection at 1×10^6 Btu/hr, the calcine area dropped from 15 m^2/g at the injection plane to 10 m^2/g at S-5 (not shown). It is notable that in contrast to the other sorbents, furnace calcine from Longview $Ca(OH)_2$ has never exhibited a greater surface area than the uncalcined feed.

Genstar dolomitic hydroxide. The surface area of Genstar injected at the burner fell from its original 20 m^2/g to less than 10 m^2/g. Figure 22 illustrates that, in contrast, injection near 2200°F yielded a calcine area of 30 m^2/g which was stable throughout the region where sulfation could occur. One sample from the plane of injection, taken with an altered sampling procedure, had an area of 68 m^2/g. Samples subsequently taken in parallel with the two methods did not show a consistent difference in area or composition. The variations at the injection plane are therefore attributed to sensitivity to probe and injector positioning. Properties of the calcine from S-4 injection either without or with SO_2 present are shown in Figures 23 and 24. (Note that these results for sulfation also appear in the discussion of in-probe reaction—see Figure 7.)

The high calcium utilization of the Genstar is ascribed to the production of surface area by dehydration of $Mg(OH)_2$, which does not itself react with sulfur in the furnace environment. This idea is supported by the following.

One of the properties of the Genstar $Ca(OH)_2$-$Mg(OH)_2$ is that heating of the sorbent in the laboratory substantially increases the specific surface area. The data in Figure 25 are the results of an experiment in which the Genstar sorbent was subject to prolonged heating at either 115 or 300°C in a stream of dry N_2. Heating at 300°C for about 11.5 hr raised the surface area from 20 to 114 m^2/g and gave a simultaneous reduction in weight of about 12%. Heating up to a total of 13.4 hr caused no further change in either surface area or weight. Results obtained at 115°C for a total of 2 hr of heating showed virtually no change from the surface area or weight first observed.

Notations near the right-hand margin of Figure 25 allow one to compare the observed reduction in weight at 300°C with that which would have occurred if half of the water of hydration had been removed or if all had been removed to produce in the first instance either CaO-$Mg(OH)_2$ or $Ca(OH)_2$-MgO and in the second instance CaO-MgO. Obviously the weight loss corresponds much more nearly to loss of half of the water. Heating at 600°C to complete dehydration yielded a surface area of 50 m^2/g.

If only one of the hydroxides lost water, it was more likely to be $Mg(OH)_2$ than $Ca(OH)_2$. This idea is confirmed by thermodynamic data from the JANAF tables, which are shown in Figure 26 as the equilibrium water dissociation pressures of $Mg(OH)_2$ and $Ca(OH)_2$ at various temperatures. At 300°C the dissociation pressure of $Mg(OH)_2$ is about 3.0 atm and that of $Ca(OH)_2$ only about 0.003 atm.

Studies of the Longview $Ca(OH)_2$ at 300°C have revealed a marked difference in properties from these observed for the Genstar $Ca(OH)_2$-$Mg(OH)_2$. Heating at 300°C for 6 hr changed the specific surface area of the $Ca(OH)_2$ only from 17.0 to 17.4 m^2/g and the associated loss in weight was only 0.1%. This observation tends to confirm the conclusion that only the $Mg(OH)_2$ in the Genstar sorbent is dehydrated at 300°C. Heating of the Longview to complete dehydration in the laboratory has not resulted in significant area increase over the raw material.

Surface area and calcium utilization. Table 9 lists the BET areas of calcines from the tests just discussed. The area given is for calcine sampled below 2200°F in the case of burner injection, or one level below the injection plane for other cases. Also listed are the calcium utilizations (based on SO_2 reduction) observed for the analogous tests with coal. Undoubtedly the sulfation and calcination processes are parallel and interdependent when calcination occurs below 2200°F. In addition, the utilization would be dependent on the nature as well as the magnitude of surface area (e.g., pore size distribution). Figure 27, however, shows a reasonable correlation between calcine surface area and utilization.

CONCLUSIONS

The applicability of furnace sorbent injection to a given situation depends ultimately on economic factors as well as required and achievable levels of SO_2 control. The results of the present study are intended to: a) provide a basis for the evaluation of removals achievable with furnace injection of commercially available sorbents, either alone or integrated with post-furnace treatment; and b) provide a foundation for understanding and improving the process. Conclusions from the present work are:

- SO_2 removal is a post-flame process that occurs via the formation of $CaSO_4$ in an oxidizing environment.

- The level of SO_2 removal is dependent on sorbent type (limestone, dolomite, hydroxide) with the hydroxides being more effective than the carbonates. Reductions observed with injection near 2200°F were:

  limestone: 40% SO_2 removal at Ca/S = 2
  dolomite: 55% SO_2 removal at Ca/S = 2
  calcium hydroxide: 50 to 60% SO_2 removal at Ca/S = 2
  dolomitic hydroxide: 70 to 80% SO_2 at Ca/S = 2

- The SO_2 removal with limestone depends on the initial source of the limestone. The more amorphous limestone with moderately high initial surface area exhibited a higher temperature sensitivity than the more crystalline carbonate. SO_2 removals approaching 60% at Ca/S = 2 were achieved with injection near 1900°F. This phenomenon could be difficult to exploit in many boilers due to rapid temperature decay in the convective passes.

- Calcine surface area appears to be one of the key parameters in the SO_2 capture process. The pilot-scale results exhibit a good correlation between the calcine surface area (at a temperature where $CaSO_4$ can form) and the level of SO_2 removal.

- Calcine surface area is highly dependent on the calcination temperature history; for furnace injection, conditions appear to be primarily controlled by sintering. Surface areas of the dolomitic, pressure-hydrated lime can vary from 10 to 35 m^2/g depending on the temperature history during the calcination process.

- Sulfation times appear to be relatively rapid with little additional sulfation occurring as the residence time in a temperature region between 2200 and 1600°F is increased beyond 1 sec. However, the very low injection temperature required to optimize capture with a sorbent such as Marianna could pose a dilemma: it is in this region of a boiler that temperature decay would be rapid, and residence time very short.

- For all sorbents investigated, temperature appears to be a more important parameter than residence time.

- Optimum temperature for SO_2 removal is in the range of 1900 to 2150°F, the lower temperatures corresponding to carbonates and the higher temperatures corresponding to hydroxides. An optimum occurs because of the interaction between sintering of the calcine surface and the kinetics of the SO_2 removal: at high temperatures SO_2 removal diminishes due to the loss of reactive surface area caused by sintering, and at lower temperature decreased reaction rates result in lower SO_2 removals (either reaction rate or solid diffusion).

- Preliminary results using precipitated carbonates (BET surface area ~21 m^2/g) yield SO_2 removals approaching that of the hydroxides.

- Limestone particle size, when varied over the range available with conventional grinding equipment has little effect on overall SO_2 removal. However, as noted above, very fine precipitated carbonates yield relatively high SO_2 removals.

- Modifying the sorbent injection airstream to contain CO_2 levels simulating the use of flue gas for transport had no effect on the SO_2 removal.

These results are expected to be useful in an assessment of the role a DSEC process may have in an overall acid rain control strategy.

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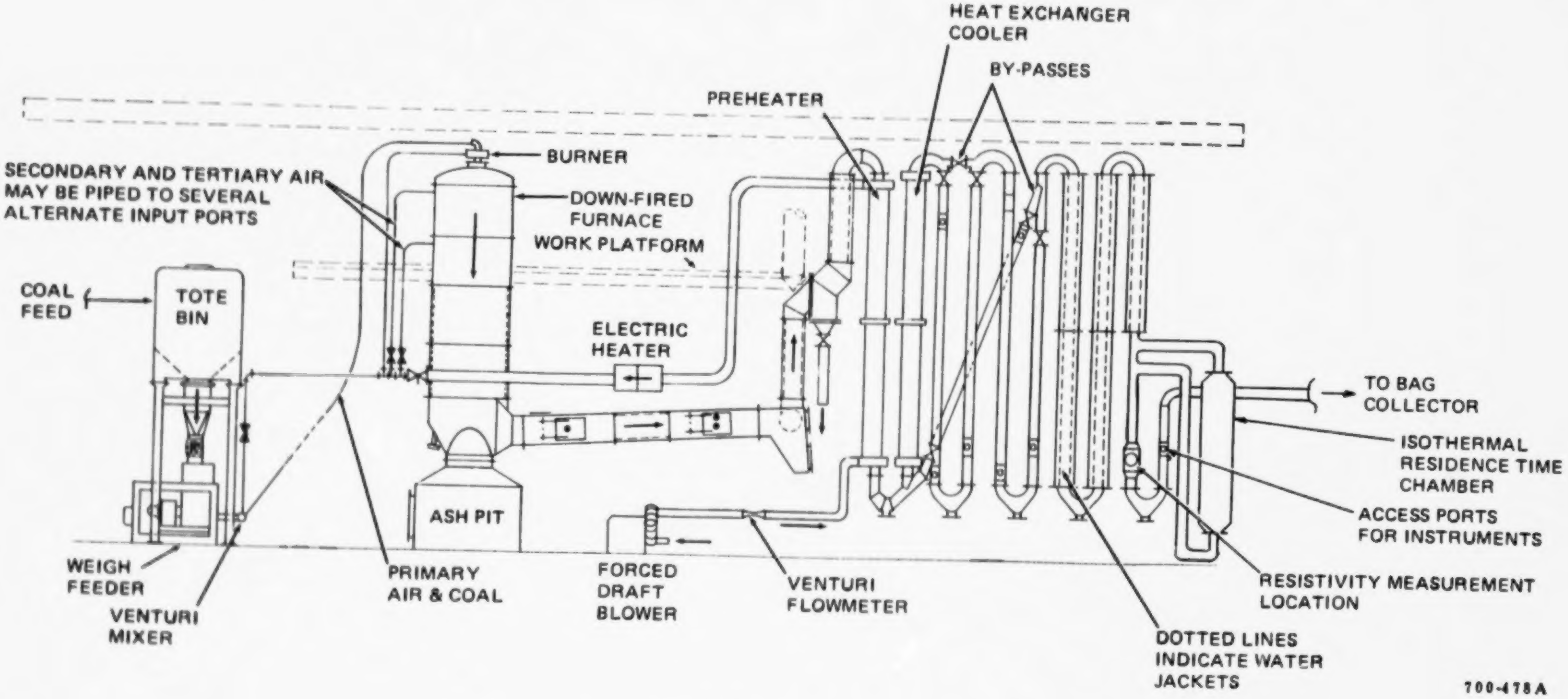
HEAT EXCHANGER
COOLER
BY-PASSES
PREHEATER
SECONDARY AND TERTIARY AIR MAY BE PIPED TO SEVERAL ALTERNATE INPUT PORTS
BURNER
DOWN-FIRED FURNACE
WORK PLATFORM
COAL FEED
TOTE BIN
ELECTRIC HEATER
TO BAG COLLECTOR
ISOTHERMAL RESIDENCE TIME CHAMBER
ACCESS PORTS FOR INSTRUMENTS
ASH PIT
WEIGH FEEDER
VENTURI MIXER
PRIMARY AIR & COAL
FORCED DRAFT BLOWER
VENTURI FLOWMETER
RESISTIVITY MEASUREMENT LOCATION
DOTTED LINES INDICATE WATER JACKETS
700-478A

Figure 1. Overall view of the pilot combustor.

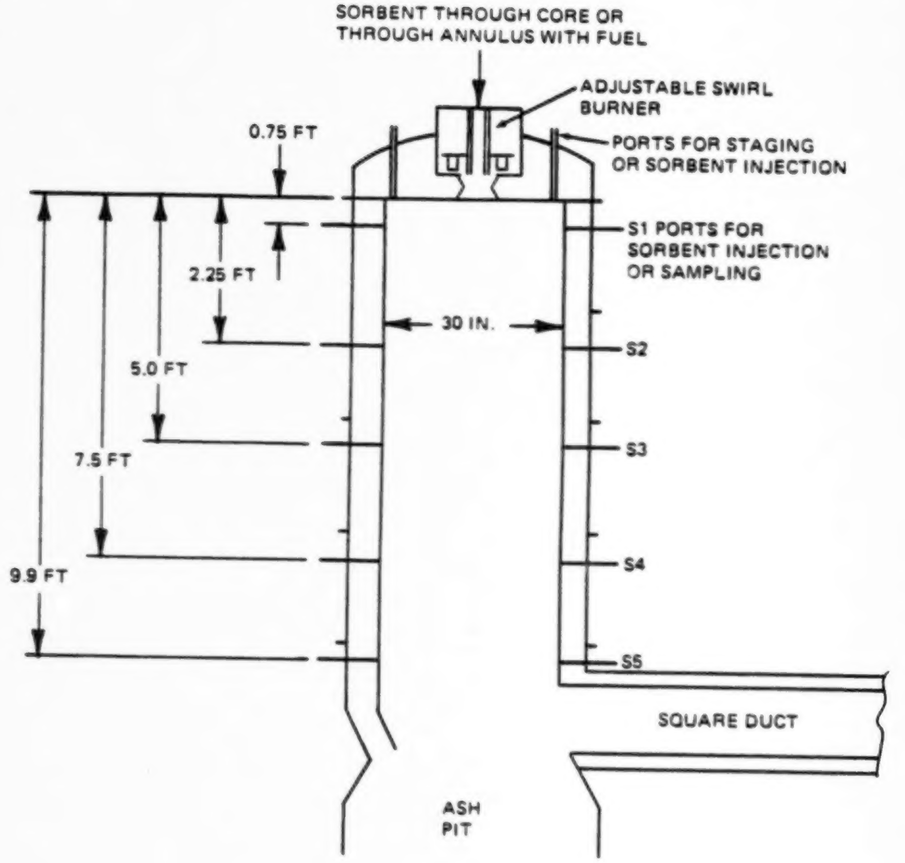
SORBENT THROUGH CORE OR THROUGH ANNULUS WITH FUEL
ADJUSTABLE SWIRL BURNER
PORTS FOR STAGING OR SORBENT INJECTION
0.75 FT
S1 PORTS FOR SORBENT INJECTION OR SAMPLING
2.25 FT
30 IN.
S2
5.0 FT
S3
7.5 FT
S4
9.9 FT
S5
SQUARE DUCT
ASH PIT

Figure 2. 10^6 BTU/hr combustor.

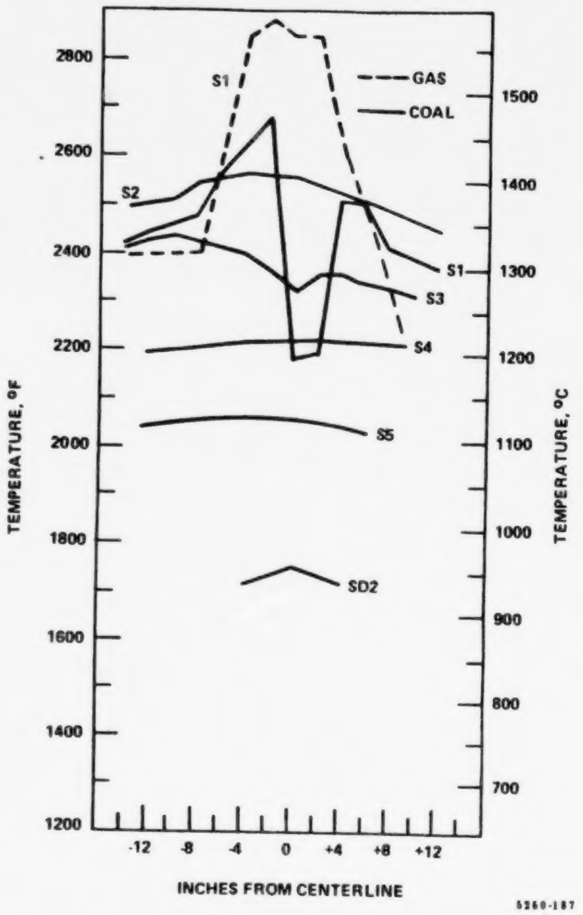

Figure 3. Radial temperature profiles, 1 x 10^6 BTU/hr.

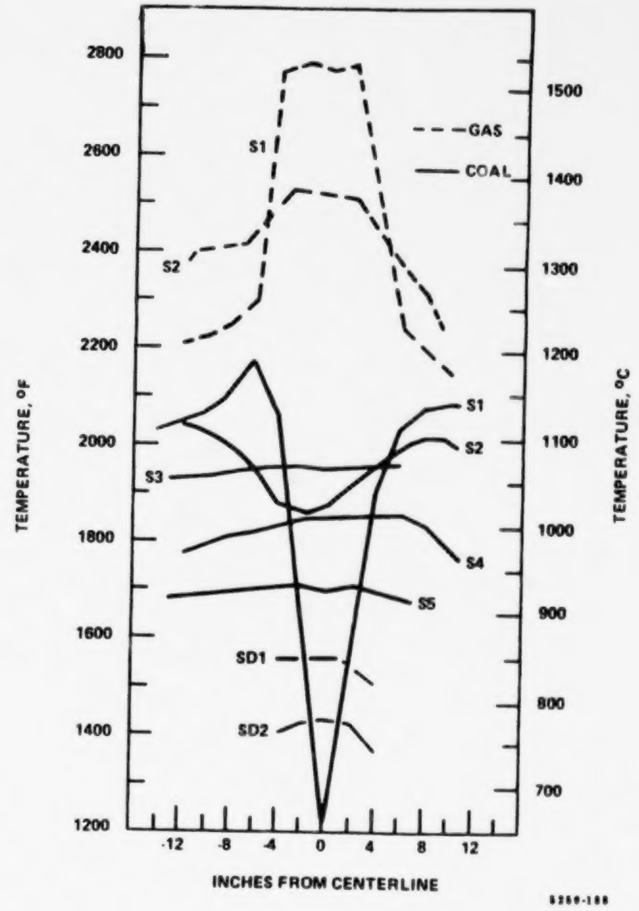

Figure 4. Radial temperature profiles, 0.6 x 10^6 BTU/hr.

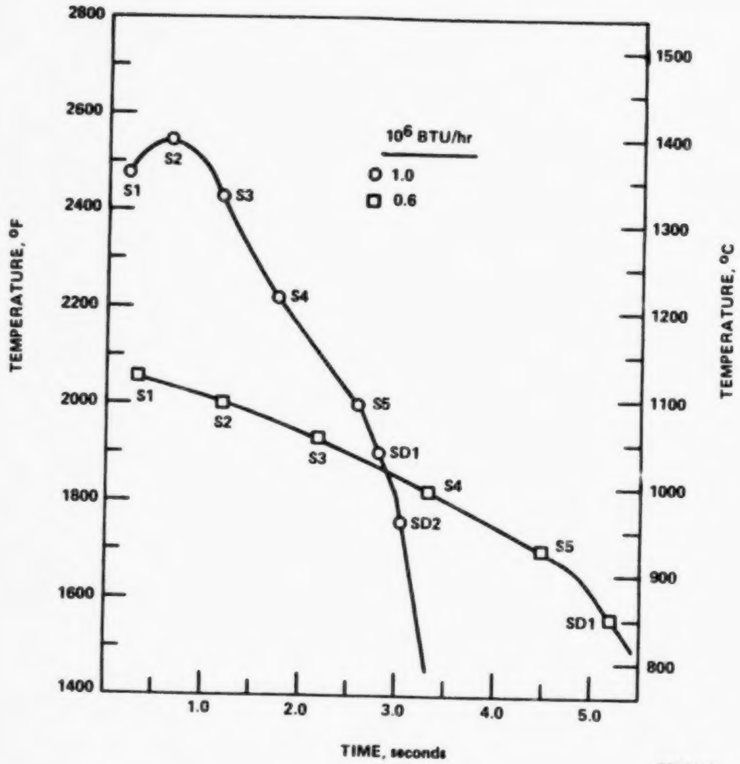

Figure 5. Temperature profile showing port locations 2 firing rates with coal.

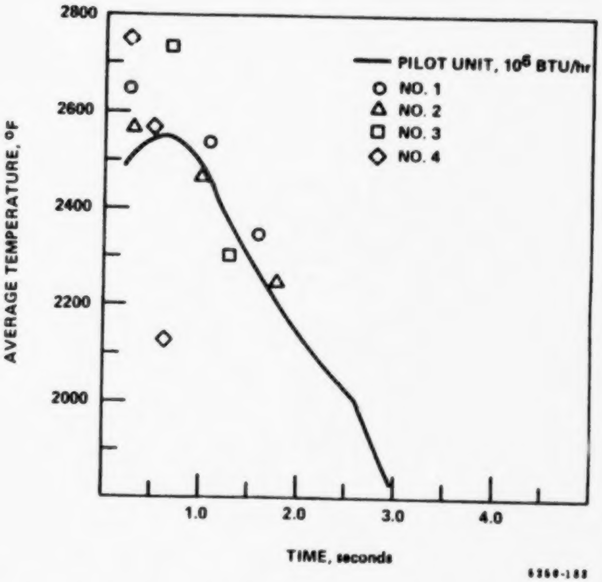

Figure 6. Temperature profiles of the pilot combustor and 4 utility boilers. The points for the boilers show average gas residences time above the top burner level, calculated from gas velocity.

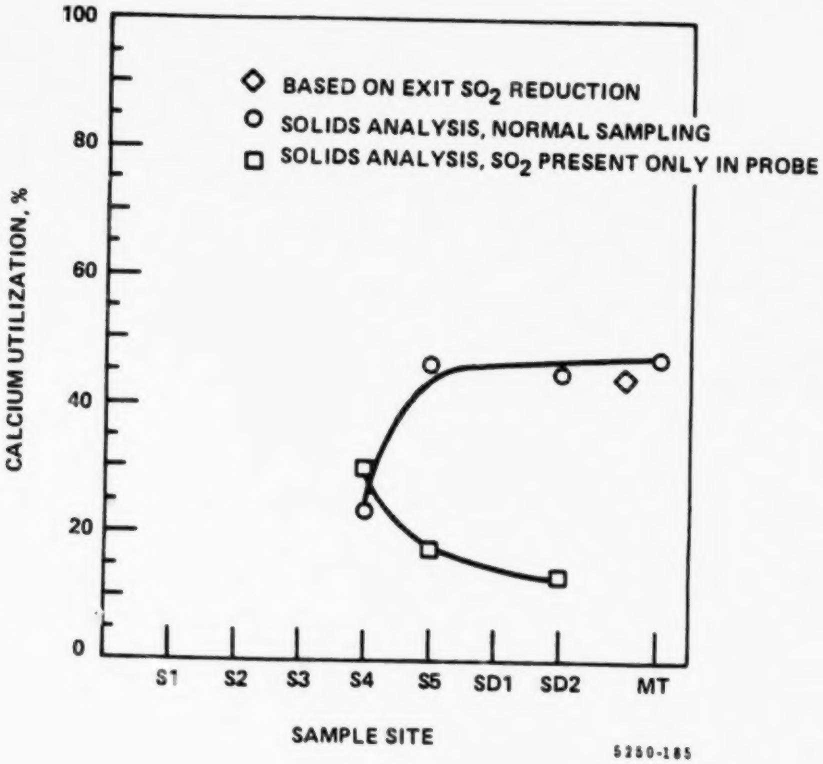

Figure 7. Calcium utilization for dolomitic lime injected at S4 with gas-firing: in-furnace compared to potential in-probe reaction. "MT" is a mass-train sampled isokinetically at about 300 °F.

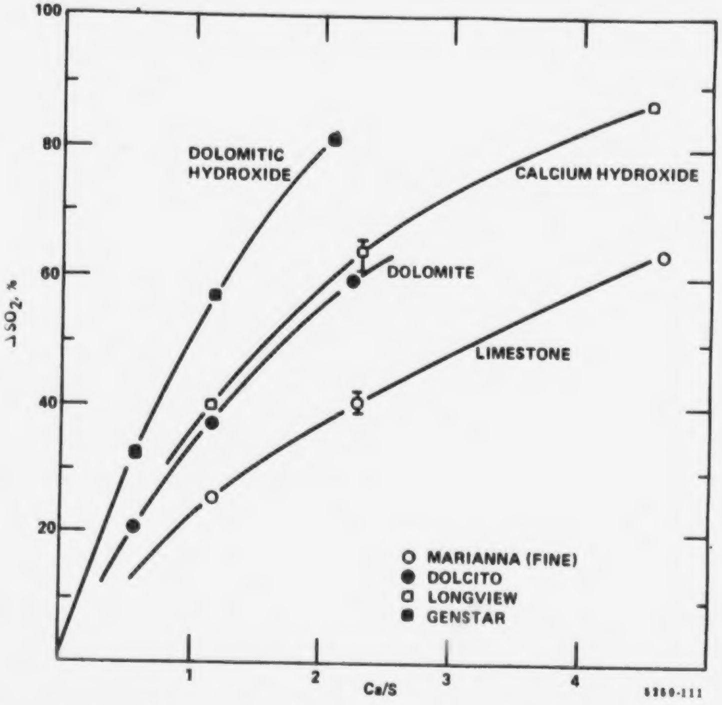

Figure 8. Performance of four sorbents. All with injection at S4 (T = 2200 °F) 1 x 10^6 BTU/hr Hallmark coal.

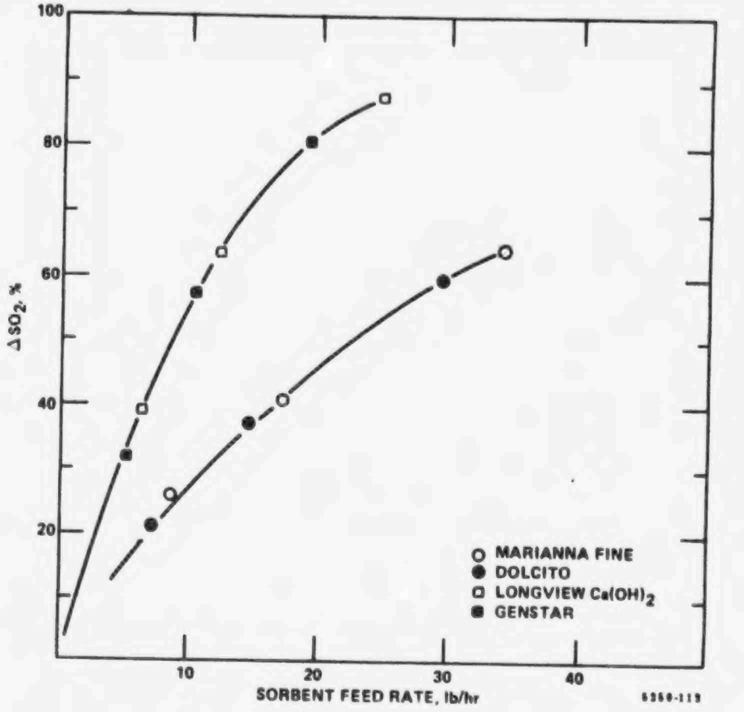

Figure 9. Comparison of sorbents on a mass feed rate basis. All with injection at S4, 1 x 10^6 BTU/hr Hallmark coal.

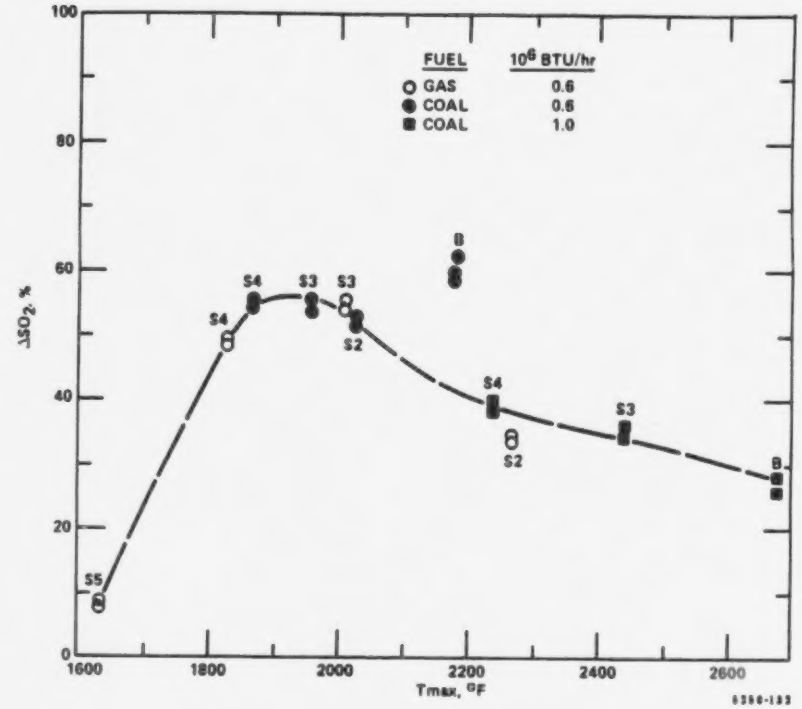

Figure 10. ΔSO_2 as a function of maximum temperature at injection for Marianna limestone. Ca/S = S 2.11 - 2.35.

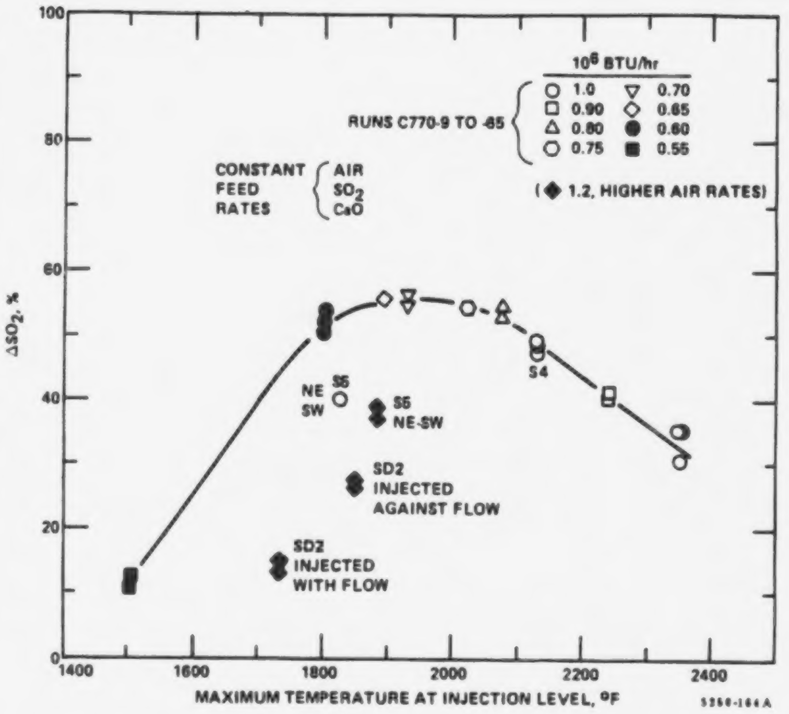

Figure 11. ΔSO_2 vs temperature of injection of Marianna limestone. All with S3 injection unless otherwise noted. Ca/S = 1.83 - 2.27.

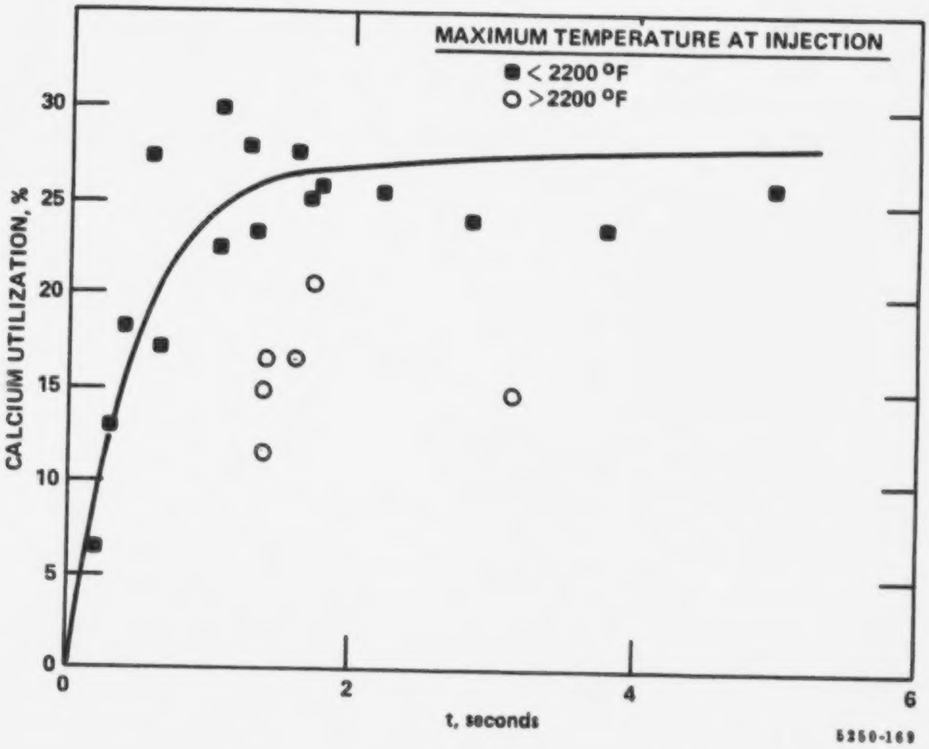

Figure 12. Utilization vs. bulk gas residence time between 2200 °F and 1600 °F. Marianna limestone, with Ca/S ~ 2.

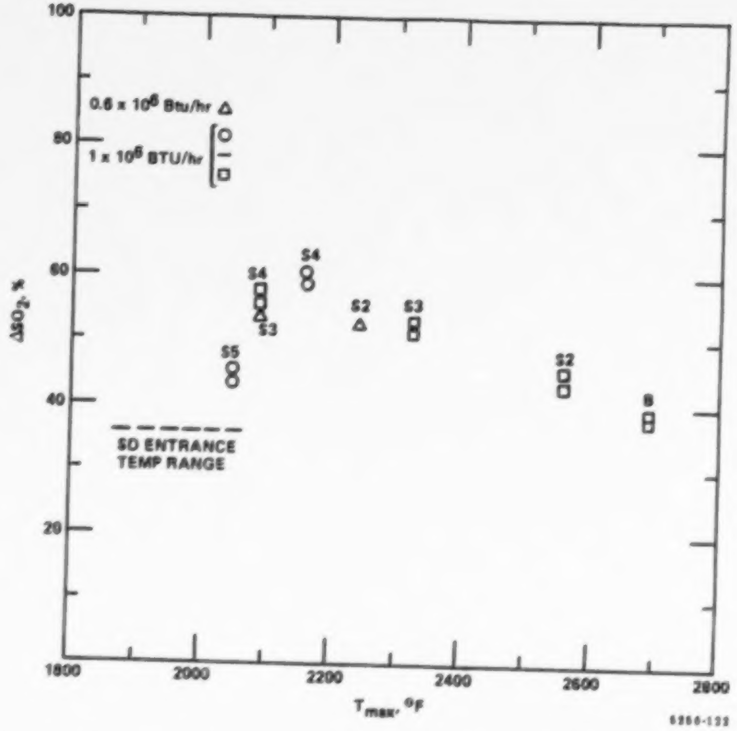

Figure 13. ΔSO_2 for Genstar PHDL: Ca/S = 1.05 - 1.16 with Hallmark coal.

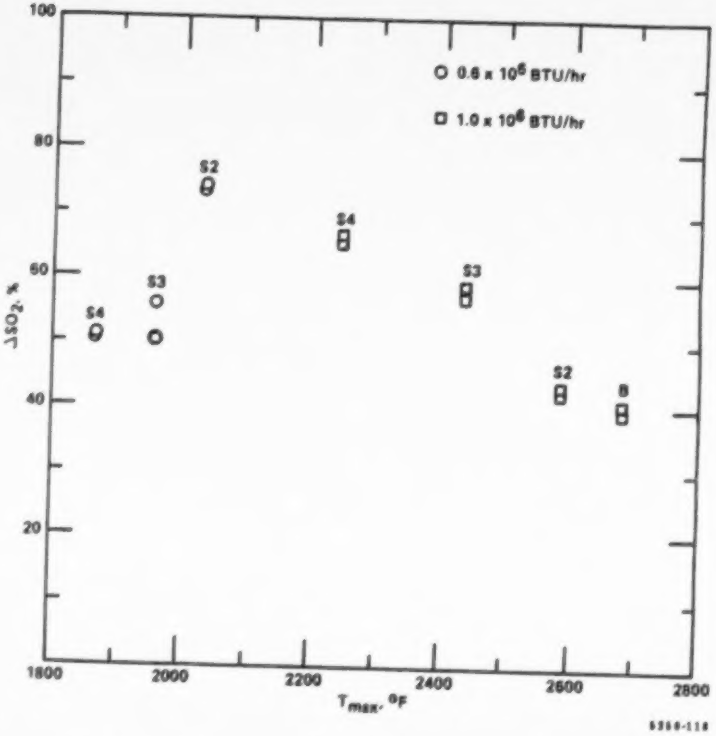

Figure 14. ΔSO_2 for Longview $Ca(OH)_2$ as a function of maximum temperature at injection with Hallmark coal. Ca/S = 2.15 - 2.25.

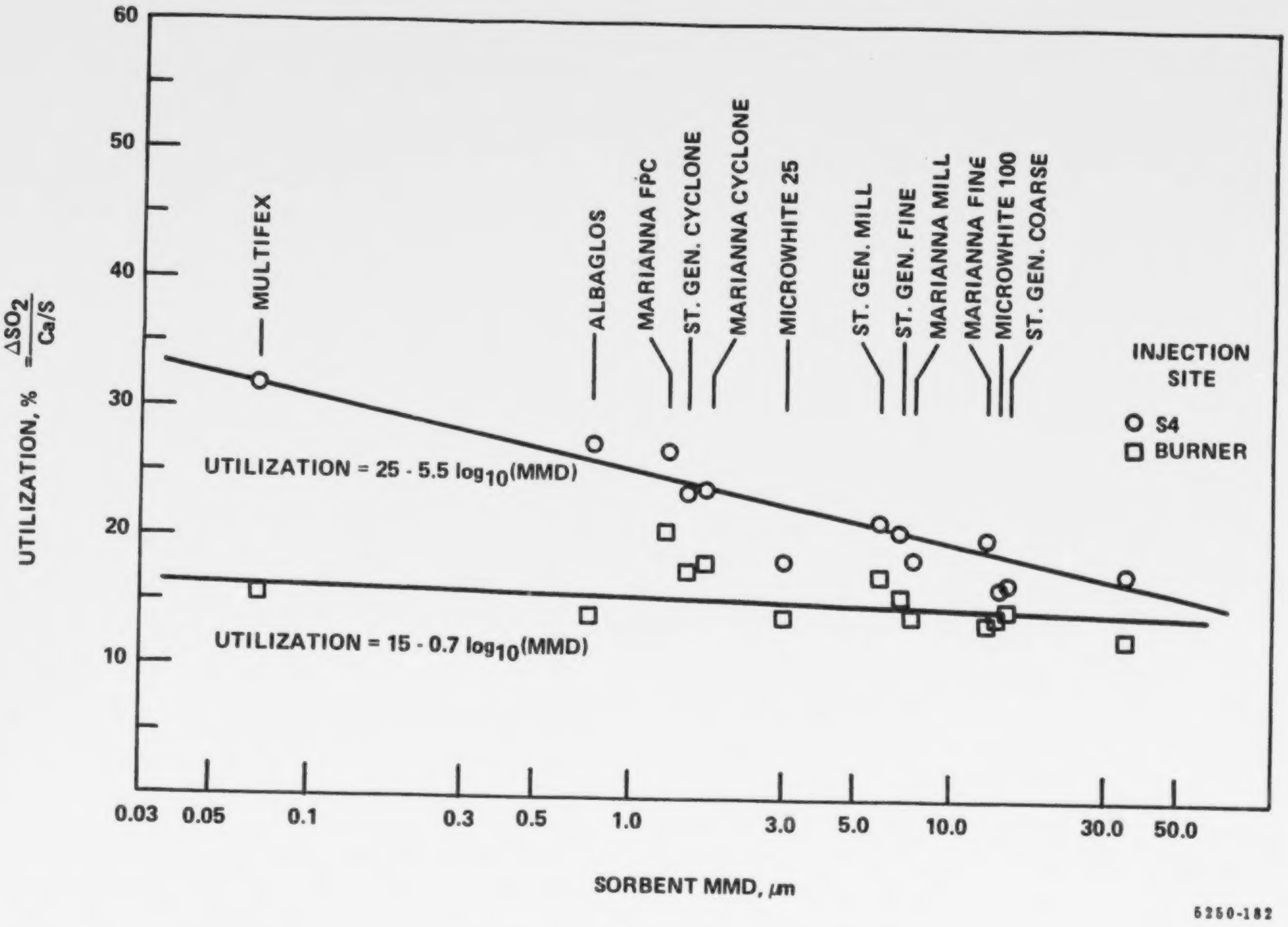

Figure 15. Utilization vs. mean particle size for calcium carbonate sorbents, Ca/S = 2. Hallmark coal, 1 x 10^6 BTU/hr.

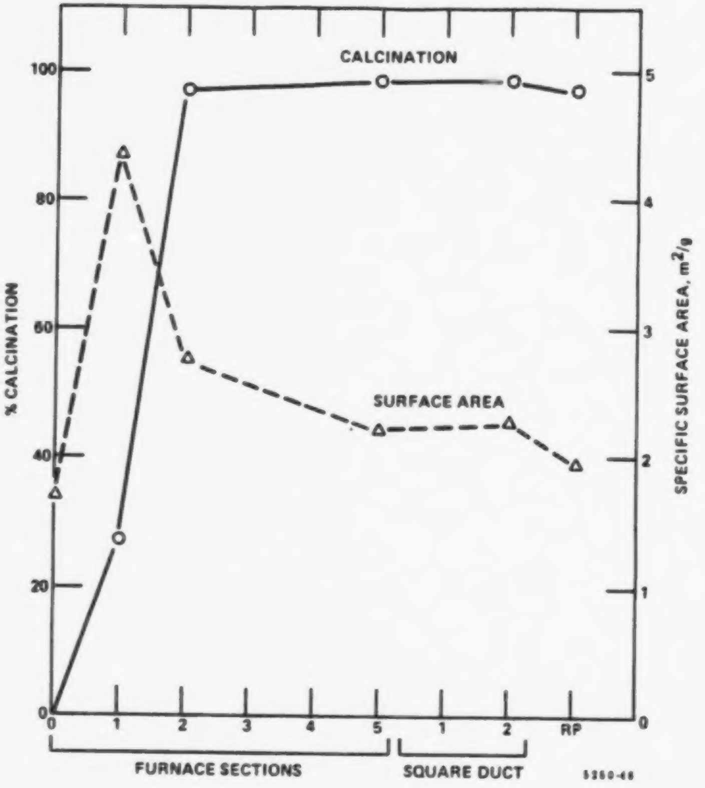

Figure 16. Characteristics of calcine sampled during burner injection of St. Genevieve limestone, 1 x 10^6 BTU/hr, 30^o swirl.

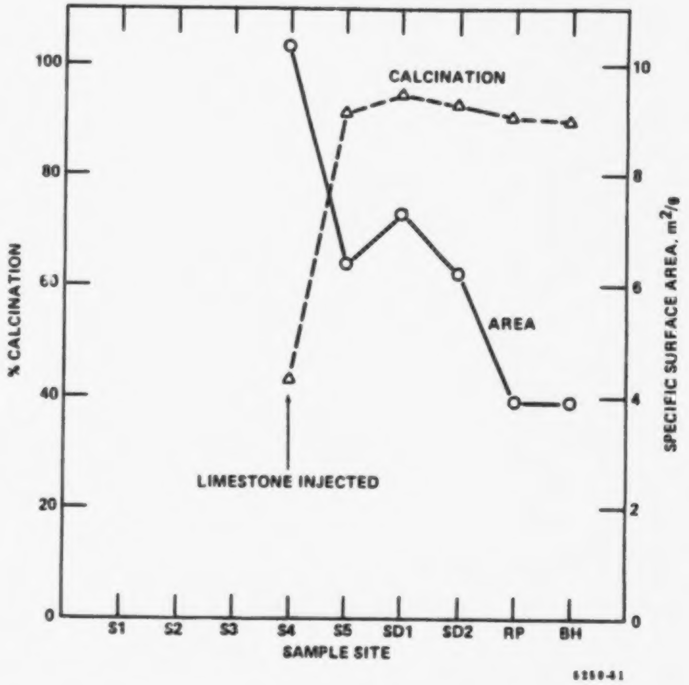

Figure 17. Characteristics of calcine sampled during S4 injection of St. Genevieve limestone, 1 x 10^6 BTU/hr.

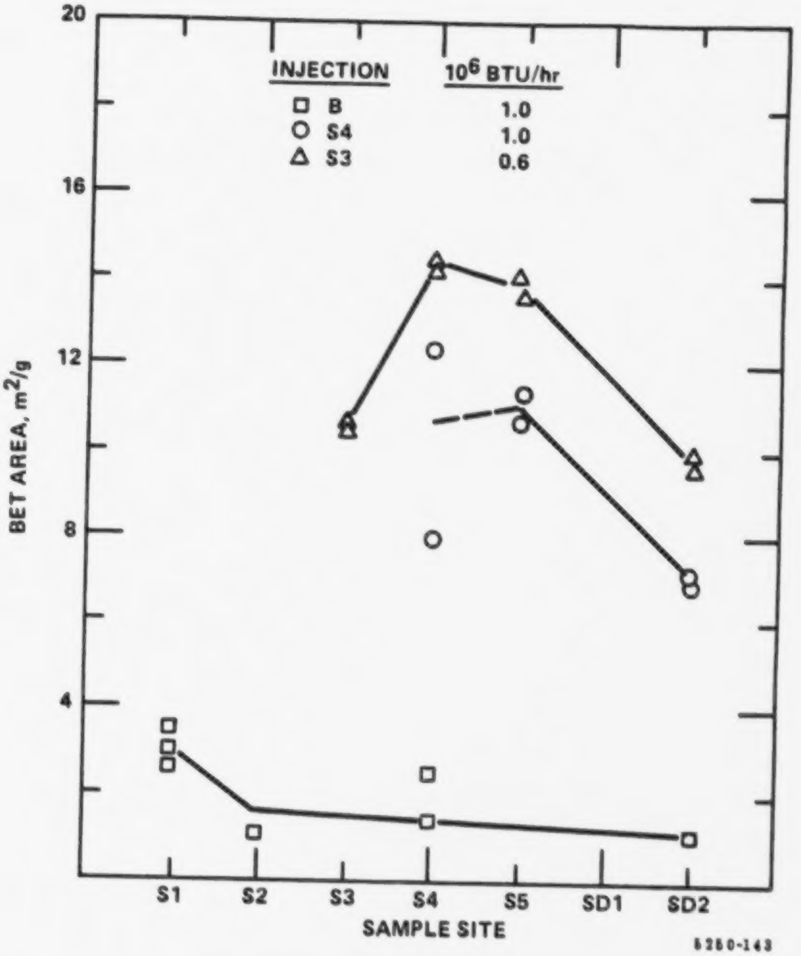

Figure 18. Surface area of calcine from injection of Marianna limestone under various conditions. Natural gas, no SO_2 present.

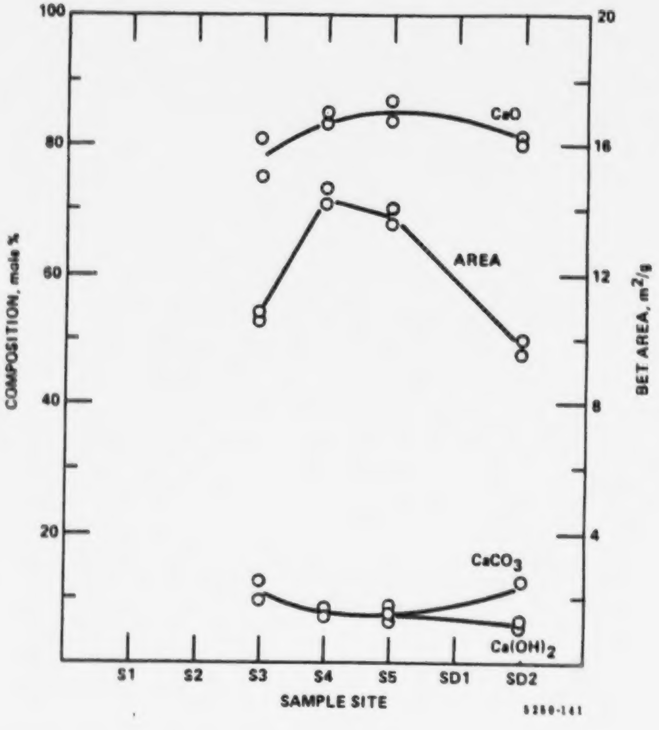

Figure 19. Properties of calcine collected during injection of Marianna limestone at S3. Gas, 0.6 x 10^6 BTU/hr, no SO_2 present.

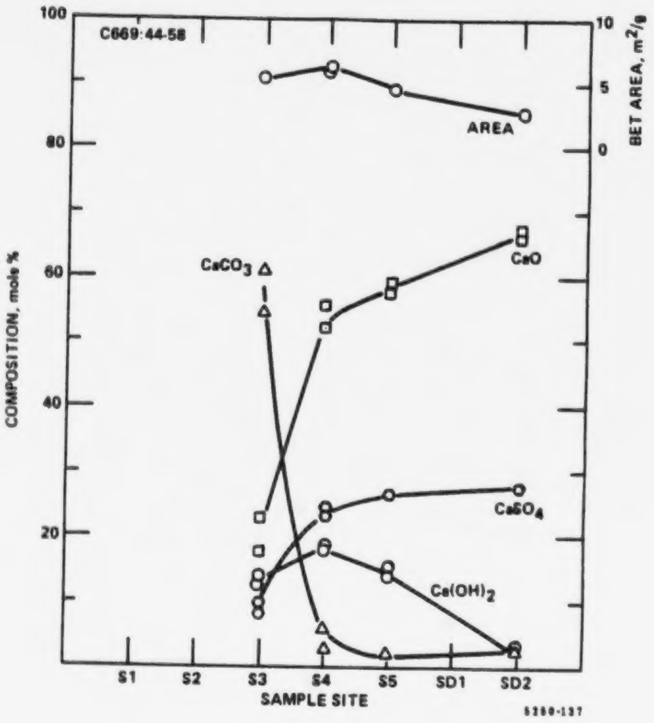

Figure 20. Properties of calcine collected during injection of Marianna limestone at S3. Gas at 0.6 x 10^6 BTU/hr, Ca/S ~ 2.

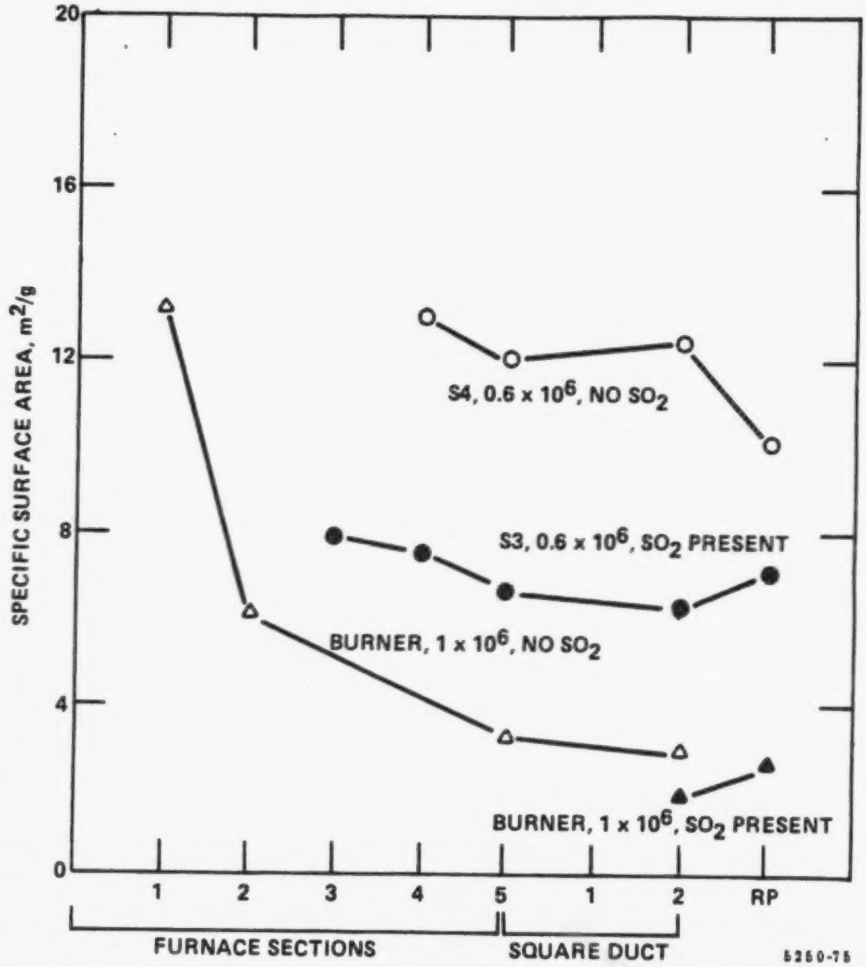

Figure 21. Comparison of BET surface areas of samples collected during injection of $Ca(OH)_2$ *at different locations and firing rates.*

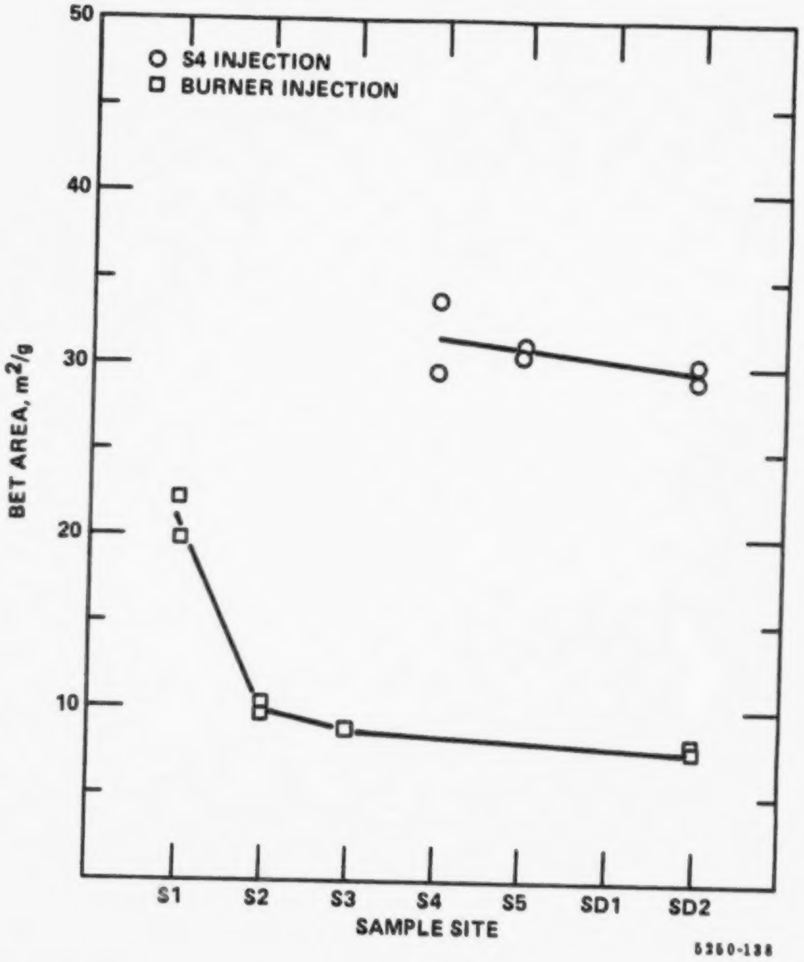

Figure 22. Surface area of calcine from Genstar PHDL injected during combustion of natural gas, 1×10^6 BTU/hr, No. SO_2 present.

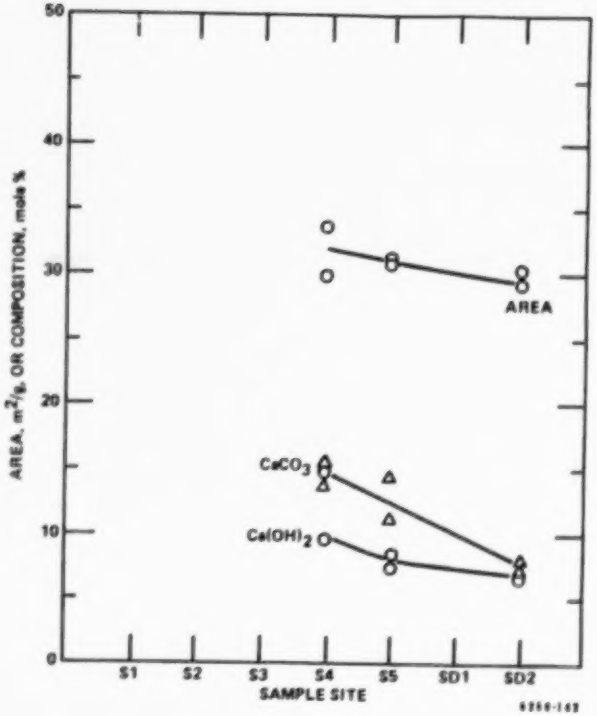

Figure 23. Properties of calcine collected during injection of Genstar PHDL at S4. Gas, 1 x 10^6 BTU/hr, no SO_2 present.

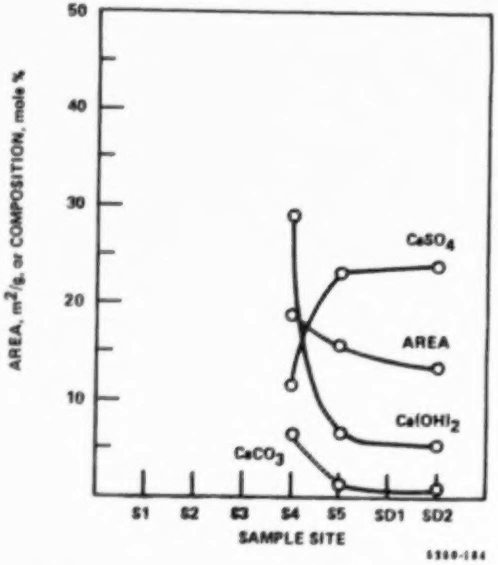

Figure 24. Properties of calcine collected during injection of Genstar PHDL at S4. 1 x 10^6 BTU/hr, SO_2 present.

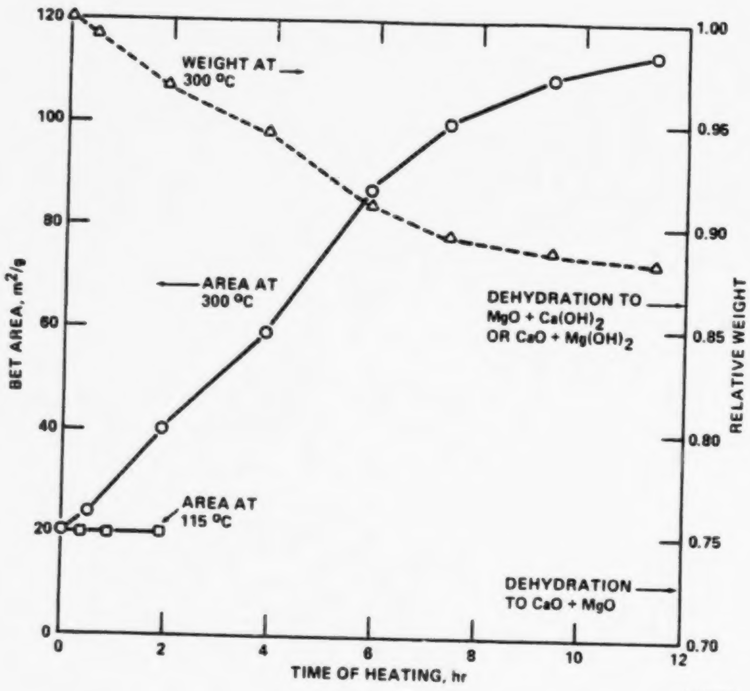

Figure 25. Effect of heating $Ca(OH)_2$-$Mg(OH)_2$ on BET surface area and weight.

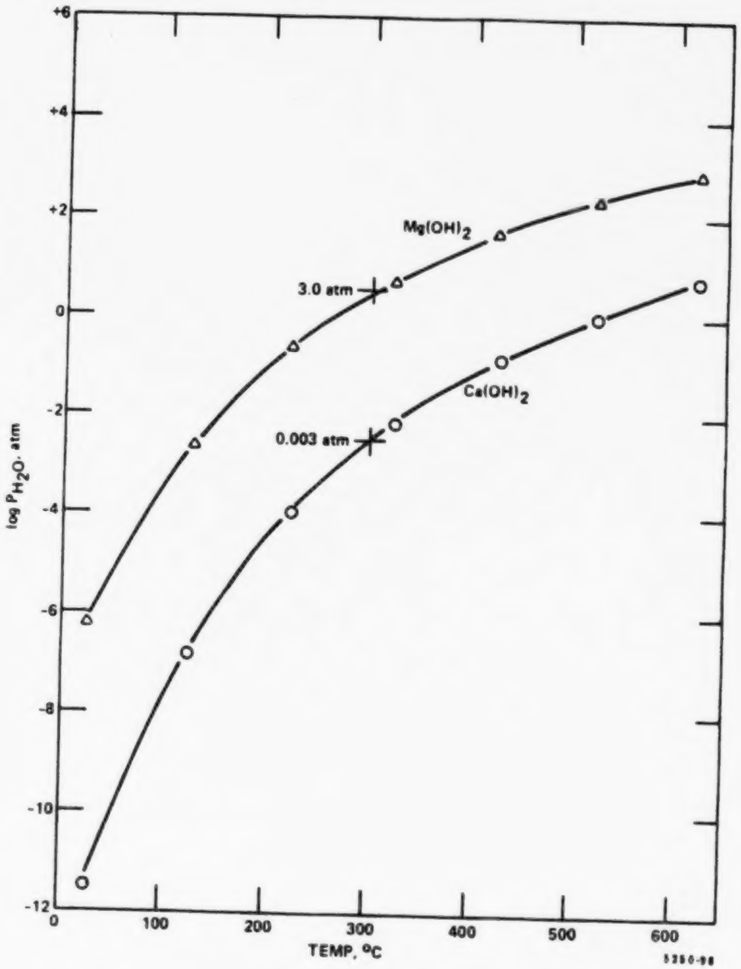

Figure 26. Thermodynamics of dehydration of $Ca(OH)_2$ and $Mg(OH)_2$.

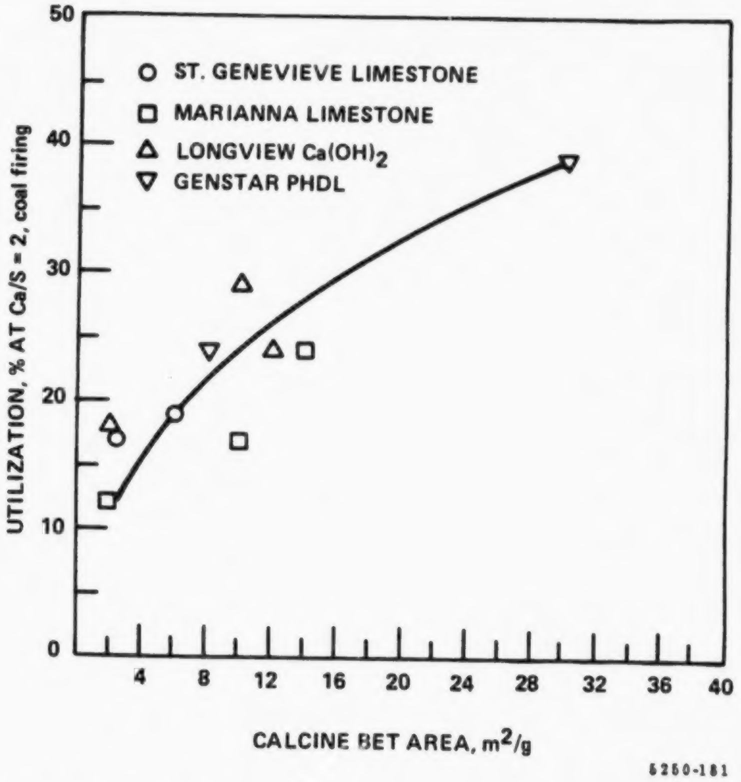

Figure 27. Calcium utilization with coal firing vs. area of calcine from analogous test with gas-firing.

Table 1. Baseline Firing Conditions

	Load	
	Low	High
Fuel rate, 10^6 Btu/hr	0.6	1.0
STA, sorbent transport air, scfm	14	14
STA, as % of total air	10	7
SR_0, overall stoichiometry	1.3-1.4	1.2-1.3
Staging	None	None
Secondary air preheat, °F	600	600
Secondary air swirl, degrees	30	30

Table 2. Comparison of Overall SO_2 Removal With Removal Near or in the Sample System, Gas-Firing

Sorbent	Flue gas temperature, °F		ppm SO_2 removed, when added[a]	
	Pre-sampler[b]	Gas sampler	With fuel	Pre-sampler[b]
Limestone	340	270	1530	72
Dolomitic hydrated lime	760	520	940	120
Hydrated lime	600	400	1280	50

---

a. During in-furnace sorbent addition, both cases.

b. "Pre-sampler" identifies the point upstream of the gas sampling probe where SO_2 is added to the flue gas. In the absence of sorbent, recovery of SO_2 injected at this point is typically 99% of theoretical, based on SO_2 and fuel feed rates.

Table 3. Recovery of SO_2 Injected Near Sample Point During Coal Firing, With or Without Sorbent Addition in Furnace

Sorbent	ppm SO_2 removed (sampled at 460°F)	ppm SO_2 increment with SO_2 injected at 675°F	% Theoretical[a]
None	none	982	102
Hydrated lime	1250	994	103
Dolomitic hydrated lime	658	965	100
Dolomitic hydrated lime	2430	989	103

---

a. Based on fuel rate, typical fuel analysis, and SO_2 feed rate.

Table 4. Analysis of Hallmark Coal
(Jefferson Seam, Alabama, Lot 1)

Coal, as-fired		Ash	
% Moisture	1.89	% Li_2O	0.04
% Carbon	74.1	% Na_2O	0.25
% Hydrogen	5.21	% K_2O	1.5
% Nitrogen	1.73	% MgO	0.69
% Sulfur	3.44	% CaO	1.1
% Ash	7.75	% Fe_2O_3	45.9
% Oxygen (diff)	5.89	% Al_2O_3	17.2
		% SiO_2	28.7
% Volatiles	37.2	% TiO_2	1.0
		% P_2O_5	0.56
Btu/lb	13,500	% SO_3	1.1

Table 5. Chemical and Physical Properties of Primary Sorbents

	St. Genevieve limestone (fine)	Marianna limestone (fine)	Longview hydrated lime	Genstar pressure-hydrated dolomitic lime
Wt % Li_2O[a]	0.01	0.02	0.02	0.01
Na_2O	0.07	0.07	0.02	0.05
K_2O	0.09	0.18	0.08	0.02
MgO	1.4	1.2	3.0	39.9
CaO	97.6	90.6	93.9	58.2
Fe_2O_3	0.18	1.2	0.30	0.11
Al_2O_3	0.30	1.7	0.43	<0.2
SiO_2	0.60	4.8	0.51	<0.1
TiO_2	<0.1	<0.1	0.10	<0.3
P_2O_5	<0.03	0.25	0.13	<0.03
SO_3	0.16	0.28	0.27	0.07
LOI, %[b]	43.4	42.2	23.7	27.2
BET area, m^2/g	1.5	6.3	21	20.0
MMD, μm	6.9	13	2.3	1.2
ρ, g/cm^3	2.69	2.71	2.24	2.28

---

a. Ignited sample.

b. As-received samples.

Table 6. Physical Properties of Different Grades of St. Genevieve and Marianna Limestones

		MMD, μm	BET area, m^2/g
St. Genevieve limestone,	coarse	15	1.1
	fine[a]	6.9	1.5
	mill	6.0	1.3
	cyclone	1.5	3.5
Marianna limestone,	coarse	35	6.3
	fine[a]	13	6.3
	mill	7.6	3.9
	cyclone	1.7	7.5
	FPC	1.3	8.3

---

[a] Chemical properties given in Table 5. This grade was air-milled to produce the finer materials.

Table 7. Properties of Other Sorbents

	Ignited		As-received		
	% CaO	% MgO	LOI, wt %	MMD,[a] μm	BET area, m^2/g
Microwhite 100, pulverized marble	96.1	1.5	43.2	18	0.8
Microwhite 25, pulverized marble	97.9	1.3	43.9	3.5	3.1
Albaglos, precipitated $CaCO_3$	95.3	0.44	44.1	0.68	7.1
Multifex, precipitated $CaCO_3$	96.0	0.54	44.2	0.07[b]	22
Dolcito, pulverized dolomite	55.8	37.2	45.8	14	2.0
Western HCPH, high-calcium, pressure-hydrated lime	94.2	1.3	25.0	3.7	17

---

[a] By sedimentation except as noted.

[b] Manufacturer's value. Sedimentation yielded 1.0 μm, apparently due to incomplete dispersion.

Table 8. Measured Values Used to Calculate SO_2 Reduction and Calcium Utilization

Calculated value	Measured values
Ca/S	- sorbent feed rate - typical sorbent analysis - molar flue gas rate (from fuel rate and analysis) corrected to 3% O_2 - baseline SO_2
Baseline SO_2 ppm	- average value of SO_2 in 5-min period preceding test, corrected to 3% O_2
Reduced SO_2 ppm	- average value of SO_2 over period 2 to 10 min after starting sorbent feed, corrected to 3% O_2
SO_2 Reduction, %	$100\left(1 - \frac{\text{reduced } SO_2}{\text{baseline } SO_2}\right)$
Calcium utilization, %	$\frac{SO_2 \text{ reduction}}{\text{Ca/S}}$

Table 9. Calcine BET Areas and Sorbent Utilizations in Analogous Gas and Coal-Fired Tests

Sorbent	Injection site	10^6 Btu hr	Gas-firing (No SO_2 present) BET area, m^2/g for T < 2200°F	Coal-firing Ca/S = 2 % Utilization
St. Genevieve	B	1.0	2.4	17
St. Genevieve	S-4	1.0	6	19
Marianna	B	1.0	2	12
Marianna	S-4	1.0	10	17
Marianna	S-3	0.6	14	24
Longview	B	1.0	3	18
Longview	S-4	1.0	10	29
Longview	S-3	0.6	12	24[a]
Genstar	B	1.0	8	24
Genstar	S-4	1.0	30	39

[a] ΔSO_2 from gas firing test. Test not completed with coal.

RECENT IFRF FUNDAMENTAL AND PILOT SCALE STUDIES ON THE DIRECT SORBENT INJECTION PROCESS

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ABSTRACT

Pilot scale experiments (2-4MW thermal) using a staged combustion air burner have shown that under optimised conditions, substantial reduction of SO2 emissions by direct injection of calcium based sorbents is possible. Various fuels including coals, ranging from sub-bituminous to low volatile bituminous, petroleum residues, and SO2 doped gas flames, have been tested with this technique and SO2 capture levels, with a Ca/S molar ratio of 2 and a calcium hydroxide sorbent, of between 70 to 80% have been achieved in cases when the peak flame temperatures were reduced to about 1250 C or lower. Both the temperature field in the furnace and the sorbent type used have been shown to strongly influence the SO2 capture efficiency with other parameters such as the SO2 and O2 concentration playing a somewhat lesser role.

Some more fundamental work has also been conducted in plug flow reactors, both isothermal and non-isothermal, to better defined calcination and sulphation rates at temperature levels ranging from 700-1300 C. The work which is only partially complete, will also examine the effect of sorbent characteristics, gas environment, and initial particle size distribution on the calcination and sulphation process. The results obtained thus far have shown that at temperatures above 1000 C, calcination is more than 80% complete in less than 200ms with CaCO3 and less than 40ms with Ca(OH)2. Sulphation also appears to be reasonably fast, reaching an asymptotic value in less than 600ms for CaCO3 when the gas temperature is between 1000 C and 1100 C. The mean particle size, in the range 3-50 µm, has a large influence on the calcium utilization for short particle residence times.

LIST OF NOTATION

ERZ - external recirculation zone
IRZ - internal recirculation zone
MC - sorbent mixed with solid fuel
SR1 - Primary zone stoichiometry
TA - sorbent injected in the tertiary air
t - time
T - temperature
η - molar percent of calcium reacted with sulphur
τ - overall reactor/sample residence time
λ - overall excess air level
Δ - % SO_2 reduction =
100 x (SO_2 without sorbent - SO_2 with sorbent)/SO_2 without sorbent

1. INTRODUCTION

The concern about emissions of sulphur dioxide and their effect on the environment is not new. However, the combination of increasing SO_2 emissions (in Europe sulphur emitted as SO_2 has gone up from 12.5 to 25 million tons per year between 1950 and 1972 [1]) and a much higher interest of the populations for their environment has led a number of countries to establish severe legislation for limiting the SO_2-emissions from fossil fuel fired systems. Such legislation is already applied or will be applied in the near future in countries like Germany, Japan, US, Sweden or the Netherlands.

For conventional combustion systems fired with oil or coal, flue gas desulphurization units are available which can reduce the potential SO_2 emissions by using lime (CaO) or limestone ($CaCO_3$), in so-called dry, wet or wet-dry processes where one essentially ends-up with a mixture of $CaSO_3$, $CaSO_4$, $CaCO_3$ and CaO, in various proportions depending upon the nature and efficiency of the process.

Not only the high investment and operational costs of these units, but also the large space required to install them between an existing boiler and a chimney is a strong limitation to the generalization of flue gas treatment, particularly for existing installations.

An attractive alternative is to use the combustion chamber itself as a reaction vessel for capturing SO_2, which can be done by injecting calcium based sorbents, $CaCO_3$ or $Ca(OH)_2$, for instance, into the combustion chamber through the burners or through specially arranged ports.

The IFRF conducted a first series of experiments in 1980 under contract to the Steinmueller Company [2]. The results were interesting enough to justify some further work in 1982 as a part of the IFRF members programme (S1-trials) and also under contract with Charbonnages de France [3] for possible further applications to a power station fired with a high sulphur coal.

More recently experiments have been carried out in plug flow reactors at the IFRF, in order to better understand the physical and chemical mechanisms of calcination and sulphation.

A large quantity of experimental data have been collected during these complementary experiments and this paper is an attempt to summarize these results and to state our present level of understanding of the phenomena involved in the direct desulphurization.

2. EXPERIMENTAL SYSTEMS

2.1 FURNACES AND BURNERS

Most pilot scale experiments were carried out with an experimental staged mixing burner previously developed by the Research Station for potential application to wall-fired boilers and schematically represented in figure 2. The main feature of this burner is the subdivision of the combustion air into four different streams: primary air, extra primary air, secondary air and tertiary air (or staging air).

- The tertiary air is injected at the periphery of the quarl through four discrete ports. Tertiary air velocity can be varied by using variable diameter inserts in these ports.
- The extra primary air is swirled with a 45 degree fixed vane swirler and flows inside the annular coal jet. This arrangement has proven to be very effective for flame stabilisation at high staging rates.
- The secondary air is swirled by means of the standard IFRF movable block swirl generator. Inserts can also be used in order to maintain sufficient secondary air velocity when highly staged combustion is considered.
- The primary zone stoichiometric ratio is defined as:

$$\text{SR 1} = \frac{\text{primary air + extra primary air + secondary air}}{\text{stoichiometric air requirement}}$$

and is a simple way to quantify the intensity of staging.

This burner is designed for a nominal throughput of 2.3MW and has been tested in previous trials where a primary stoichiometry SR 1 = 0.5 could be achieved with resulting low NOx emissions and maintenance of short and stable visible flames.

The burner was fitted to the IFRF number 1 furnace which is refractory lined with internal dimensions of 2 x 2 x 6.25m and horizontally fired (see figure 1c). For the sorbent injection experiments the furnace was equipped with eight water-cooled loops which together with heat losses provided a heat extraction in the furnace of about 50% of the total thermal input giving a flue gas temperature of 1000 ± 50 C and wall temperatures between 800 C and 1000 C.

With the staged mixing burner, the dry sorbents could be injected in three different modes:

- Mixed with the coal (MC in figures): by mixing the sorbent and its transport air with the primary air-coal mixture before the burner.

- In tertiary air (TA in figures): by injecting the sorbent in the tertiary air port at the burner. This mode of injection is applicable with staged combustion only.

- At burner periphery: when non-staged combustion is considered, by means of four injectors of small diameter (14mm) which were inserted in the tertiary air ports themselves (transport air for the sorbents is only 2% to 4% of combustion air).

Experiments have also been conducted in the IFRF vertical furnace operating as a non-isothermal plug flow reactor, see figure 1a. This furnace is 4m high, has an internal diameter of 0.6m and is refractory lined.

A gas fired burner is set at the top and its function is to generate hot combustion gases, the temperature and oxygen content of which can be respectively adjusted within the ranges 1000 C to 1400 C and 1 to 12% by means of removable cooling pipes and oxygen injection. The essential function of the upper furnace zone is to create a plug-flow with an average velocity of 1.5m/s and a well controlled temperature and gas composition.

The material to be studied is injected with an inert carrier gas (Nitrogen in practice) at the top of the "working section" of the furnace by means of a solid distributor, which spreads the solid particles across the entire width of the furnace ensuring, fast radial dispersion of the solids in the flow. The vertical position of the solid injector can be considered as the origin of the reacting flow and by inserting sampling probes in the furnace through accessible ports at variable positions downstream it is possible to follow the progress of reaction. Residence time measurements have shown that the furnace is operating as a plug-flow, i.e. without any significant back-mixing and in such a way that axial distances can be easily converted into residence times.

Studies with the new IFRF isothermal plug flow reactor have also started, see figure 1b. This reactor tube is 80mm diameter and is divided up into six electrically heated sections. The hot gases are supplied by a precombustor in which combustion of a combination of blast furnace and natural gases produces a gas similar to that achieved with coal combustion. The temperature of the gases can be varied in the range 700 - 1300 C by changing inputs and also with cooling pipes which can be inserted into the precombustor.

The gas concentrations can be altered by changing inputs and by the addition of N2, CO2, H2O or SO2. The hot gases are then injected into the reactor where the electric elements maintain a constant temperature along the reactor length.

The total gas residence time in the reactor can be varied from 150ms to about 600ms, by changing the velocity (flow rate) of the gases. By inserting a water-cooled probe into the reactor from gas and solid samples can be taken at any height inside the tube. Samples can be taken after residence times as short as 10ms. The solids are injected at the top of the reactor tube into a venturi to assure good solid and gas mixing. Solid injection rates are typically 500g/hr. The solids drawn into the probe are quenched to about 150 C with an inert gas quench. The quenching time is estimated at about 2-3ms for particles less than 20 μm.

2.2 FUELS AND SORBENTS

Three coals were used in the more recent experiments:

- a German bituminous coal from the Saar area having 1% sulphur;
- a sub-bituminous coal from Gardanne (France) having around 4% sulphur and 30% ash as mined;
- the same Gardanne coal washed down to 8% ash.

Analyses of these coals and of their ashes are given in table 1. The important feature of the Gardanne raw coal is that its ash contains 50% CaO giving it potential for significant "natural retention" of SO2 in the ash itself.

High sulphur containing (about 3.5%) solid and liquid petroleum residues have also been tested with the direct sorbent injection technique.

The analyses of the four main sorbents refered to in this paper are shown in table 1. The sorbent described as shale is extracted during the mining of the Gardanne coal and comes from layers adjacent to the coal stream. In figure 3, the particle size distributions for the sorbents tested, are shown.

3. SIMPLE BASIC CONSIDERATIONS

When a finely ground $CaCO_3$ or $Ca(OH)_2$ is injected into a flame, it undergoes calcination reactions as follows:

$$CaCO_3 \rightarrow CaO + CO_2, \text{ or} \quad (1)$$

$$Ca(OH)_2 \rightarrow CaO + H_2O \quad (2)$$

Thermodynamic considerations, confirmed by experiments, indicate that calcination starts around 800 C for (1) and around 500 C for (2), see figure 4. Usual gas temperatures in a pulverized coal flame are significantly higher and one can expect a "flash" calcination of the sorbent liberating a freshly calcined lime which can react with SO2 according to the overall chemical equation:

$$CaO + SO_2 + 1/2\ O_2 \leftrightarrow CaSO_4 \quad (3)$$

Intermediate steps involving the formation of $CaSO_3$ or the direct reaction of CaO with SO_3 for instance ought to be considered when a detailed analysis of the chemical process is required but for the engineer this equation is a simple description of the overall process.

The reaction described by equation (3) is reversible and at high temperatures, $CaSO_4$ becomes thermally unstable. Data from thermodynamic calculations and also a few experimental results on thermal decomposition of $CaSO_4$ are available in the literature and they have been plotted in figure 5 [4, 5, 6]. There is a fair agreement between calculations and experiments to show that with 4% O2 and 1000ppm SO2 in the gas phase, $CaSO_4$ is unstable above 1200 C. It is also seen that the gas phase composition has a strong influence on the stability of $CaSO_4$: in presence of 1% CO and with 1% O2 and 1000ppm SO2 in the gas phase (which is typical of what can be found in the first part of a pulverized coal flame), the limit of stability of $CaSO_4$

drops to about 1000 C. If carbon is present with CaSO4 (in the form of soot for instance) the limit of thermal stability drops below 900 C for 1000ppm SO2. Although these data are relative to systems at equilibrium, they indicate clearly that temperature must be a predominant limiting factor in the capture of SO2 by calcium in flames.

3.1 RESULTS FROM THE PLUG FLOW FURNACES

3.1.1.Calcination results

In figure 6, calcination rates for CaCO3-3 and Ca(OH)2-2 are shown for temperatures ranging from 700-1300 C. It can be seen that the rate of calcination for CaCO3 is reasonably fast for temperatures greater than 1000 C, while with Ca(OH)2, calcination is extremely fast for all temperatures examined. It is important to note that when the calcium hydroxide was calcined at 700 C and 900 C, that significant amounts of CaCO3 were quickly formed. However, at temperatures of 1100 C or higher, very little CaCO3 was found in correspondance with equilibrium considerations, see figure 4.

Also Ca(OH)2 was found in the calcined sample, even after exposure to high temperatures for long residence times. It is believed that this calcium hydroxide was reformed in the sampling probe or collection filter.

Calcination rates have also been measured in gas streams with CO2 concentrations ranging from 19% to 8.5% and H2O concentrations from 19% to 6.5%. In this range of variation, very little change in the calcination rate or final level was found.

Measurements of particle size before and after calcination indicate that some particle breakup does occur during calcination with the percentage breakup being a function of the gas temperature. With a gas temperature of 1300 C the increase in mass percent of particles less than 10 μm increased from 65% to about 85% for the Ca(OH)2 sorbent.

3.1.2 Sulphation results

In figure 7 the sulphation results from the non-isothermal plug flow reactor are shown. During these experiments the high ash Gardanne coal was injected into the reactor without additional SO2 or calcium (inherent Ca/S = 2.23). Further the shale mined between the coal seams was injected along with SO2 (Ca/S = 2.27). In both cases the potential SO2 concentration, whether from coal combustion or from direct injection was similar. The temperature distributions shown are gas temperatures as measured by suction pyrometer.

Several conclusions can be drawn from these relatively brief experiments.

At temperature levels where high concentrations of CaSO4 are thermodynamically stable, and high enough for rapid calcination, the rate of sulphation is reasonably fast reaching an asymptotic value after about 0.5s. If the shale (CaCO3) is injected at a temperature where the formation of CaSO4 is limited by what are probably thermodynamic reasons, curve 3 in figure 7B, as the temperature drops below 1000 C, the sulphur capture level approaches that of curve 4b. However, if the sorbent is exposed to a high enough temperature, somewhere between 1100 C and 1200 C, then the capture efficiency seems to be limited to a level considerably below that achieved at temperatures where the sorbent is always below 1100 C, see curves 1a, 2a, 3a, 4a in figure 7.

Another important conclusion is that, especially at temperatures where the rate and final level of $CaSO_4$ formation are maximized (T<1100 C), neither the mineral matter in the coal ash nor the combustion of the organic fraction of the coal have a predominant effect on the formation of $CaSO_4$.

In figure 8 some initial sulphation results from the isothermal reactor are shown. These experiments where done with an initial SO_2 concentration of 2000ppm and a Ca/S ratio ranging from 1.7 to 2.1. These samples have been collected when the furnace was set up to study calcination and consequently the residence times are quite short; 150ms for $Ca(OH)_2$ and about 300ms for $CaCO_3$. For both $CaCO_3$ and $Ca(OH)_2$ and with the gas composition snown in figure 8, the optimum temperature for sulphur capture in these short residence times is between 1000 and 1100 C. At temperatures below 1000 C the fraction of calcium present as $CaCO_3$ increases, reducing the amount of calcium available for reaction with sulphur. In both cases the increase of $CaCO_3$ corresponds to a sharp drop in $CaSO_4$. The percent $CaCO_3$ present at 900 C is much greater with the $CaCO_3$ sorbent than with the $Ca(OH)_2$. This perhaps can be explained partially by the fact that initially the $CaCO_3$ reformed after calcination of $Ca(OH)_2$ would be predominately at the particle surface which is where the reaction with sulphur occurs, while in the case of the $CaCO_3$ sorbent the uncalcined material is probably well dispersed throughout the particle.

Also the data in figure 8 indicates that at temperatures below 1000 C, $CaSO_3$ begins to be the major calcium-sulphur form present. This again appears to be related to thermodynamic considerations which show that $CaSO_3$ will begin to decompose at about 950 C [7].

The calcium utilization curve with a $Ca(OH)_2$ sorbent shown in figure 8 has a minimum at between 1000 C and 700 C. The reason for this appears to be the predominance of $CaSO_3$ at 700 C, while at above 900 C $CaSO_4$ is the major calcium-sulphur compound found.

$Ca(OH)_2$ sorbents of various mean particle sizes (49, 24 and 3 μm) have also been injected into the isothermal reactor. With an overall particle residence time in the reactor of about 150ms, a significant difference in sulphation level was found at 1100 C and 700 C, see figure 9. From these initial tests it is uncertain if the ultimate calcium utilization level is a function of the particle size, or if only the sulphation rate is changed.

In figure 9, the curves between 700 and 1000 C are drawn as a dashed line due to uncertainty about the nature of the curve in this range, see figure 8. Also in figure 9 the percentage $CaCO_3$ originally present in the $Ca(OH)_2$ sorbent for the different sizes are shown alone with the mass mean particle size and the measured BET surface areas.

In conclusion, the smaller scale isothermal and non-isothermal work performed at the IFRF up till now indicates that a relatively narrow temperature range exists (1000 C - 1100 C) where the calcination and sulphation processes are optimized so that high capture efficiencies can be achieved in short times (< 600ms), and with small $Ca(OH)_2$ particles perhaps much faster.

At temperatures above 1100 C the sulphation process is limited by equilibrium considerations and very likely dead burning, whilst at temperatures below 1000 C the calcination rate with CaCO3 or CaCO3 formation with Ca(OH)2 sorbents appears to limit sulphation. At temperatures less than 900 C, CaSO3 becomes the major sulphur calcium compound formed, at least for short residence times.

3.2. PILOT PLANT SCALE RESULTS

3.2.1 Effect of flame temperature and injection location

One major controlling parameter for the capture efficiency of sulphur by direct injection of calcium based sorbents in or near a flame is flame temperature. In figure 10 the correlation between peak flame temperature and the percent SO2 reduction is shown as measured when the fuel and sorbent were mixed during various pilot plant scale experiments (2.5 MW thermal input). It is important to note that most of these data have been generated during experiments in furnace number 1 where the average residence time is about 6 seconds, and the residence time at temperatures of about 1050 C or less, is typically about 2 seconds, see figure 12. This again indicates that exposure of the sorbent to high temperature causes a change (sintering) in the reactivity of the stone, so that its capture efficiency is reduced when the gas temperature decreases to temperatures thermodynamically suitable for sulphation. This appears to hold true for solid fuels without any appreciable mineral matter, such as petroleum coke, see figure 10.

In figure 11, the effect of peak flame temperature on the sulphur capture when the sorbent is injected in the staging air stream located as in figure 1. In this case there is no longer a direct relation between peak temperature and capture efficiency although a trend of decreasing capture with increasing peak temperature still exists.

The probable reason for the increased capture values and reduced dependence of sulphur capture on flame temperature can be seen in figure 13.

When the sorbent is mixed with the staging air, the jet containing the sorbent is heated by entrainment of both external recirculation and flame gases and as can be seen in figure 13, the temperature of the bulk of the staging air is much colder than the flame. In general, the temperature of the tertiary air jet for these flames reaches a maximum at approximately the same temperature as the external recirculation gases. It is believed that an indirect relation between peak flame temperature and sulphur capture arises because a portion of the staging air jet does mix directly with the flame and also some calcium carried back in the external recirculation zone is entrained directly into the high temperature flame zone between the staging air jets.

When the flame temperatures are low as in figure 13c, then the benefit of injecting the sorbent in the tertiary air is decreased, and high capture values can be obtained when the coal and calcium are premixed.

3.2.2 Effect of sorbent type

Another important parameter that has been found to control the SO2 capture efficiency of the calcium sorbents is the sorbent type. In figure 14, the results of tests with various CaCO3 sorbents and a calcium hydroxide are shown. Typically Ca(OH)2 gives twice the capture of CaCO3 based sorbents. It is believed that this property can be attributed to a greater active surface of the calcined hydroxide when compared to the carbonate.

3.2.3 Effect of fuel type

The measured SO2 reduction when a calcium hydroxide sorbent was injected into a staging air stream of various liquid, solid, and gaseous fuels is shown in figure 15. In general, these results can be explained by the measured peak flame temperatures and/or the sulphur content of the fuel. With fuels containing a high sulphur concentration and those giving lower flame temperatures, the sulphur capture was high. When flame temperatures were high or when the fuel sulphur content was low then the capture efficiency was reduced.

Particularly when the sorbent is injected so that the majority of the calcium passes around the high temperature flame zone there is no evidence that fuel mineral matter plays an important role.

3.2.4 Effect of excess air

With Gardanne coal the excess air was varied from 5% (with unwashed coal) up to 50%. Figure 16 indicates that for the washed coal a high excess air has a strong beneficial effect on the SO2 capture when Ca(OH)2 is used irrespective of the sorbent injection mode: the SO2 capture is increased by a factor 1.4 to almost 2 when the excess air factor is increased from 15 to 50%. Axial flame temperature measurements were taken for these three excess air levels in order to ensure that this positive effect was not the result of a decreased temperature at high excess air. The same beneficial effect of a high excess air on SO2 capture was also observed with "natural retention" as seen in figure 16. The unwashed coal was fired at very low excess air (5%) and the natural retention dropped dramatically from 40% at 15% excess air to 20% at 5% excess air. With 50% excess air the natural retention increased to 50%. The same trend was again observed when supplementary injection of Ca(OH)2 was carried out and figure 16 shows the same effect of excess air for washed and unwashed coals, for natural or artificial retention and for different sorbent injection modes.

3.2.5 Effect of SR1

One of the major objectives of the pilot plant scale experimental work was to investigate the effect of staged combustion upon the efficiency of SO2 capture. The results indicate that based on the time-temperature or chemical history of the sorbent particles when mixed with the coal, staged flames generally do not have a direct advantage when compared to non-staged flames. The advantage to staging the combustion air is that it allows the sorbent to be injected in the staging air and thus the sorbent can bypass, at least partially, the high temperature flame zone.

4. EXTENSION TO LARGER SCALE

Although uncertainties about temperatures fields and flame interaction and mixing in large multi-burner water tube boilers make direct extension of bench and pilot scale to the large scale difficult, by using some general information about large boilers and the pilot scale data available from the

IFRF and other organizations, some conclusions about the best method of sorbent injection into large boilers can be drawn.

In wall-fired bituminous coal boilers the following general observations are supported by either experimental data or modelling considerations.

- For large burners (> 30MW), the high temperature flame zone is much longer and gases/solids are in-flame for a longer time than the 2.5MW flames at the IFRF scale.

- Some mixing of gases between burners will occur.

These two observations would indicate that most of the gases/solids travelling through the combustion zone of a boiler are at temperatures above that at which sulphation will occur and dead burning can reduce the sorbent reactivity, i.e. T > 1200 C, so that when the temperature drops below 1200 C the capture efficiency will be reduced. It is uncertain if putting the sorbent into tertiary air streams around the burner will be as effective on a large boiler as in the IFRF furnace due to mixing of products between different burner rows.

The bench scale results have shown that when the sorbent is injected into an optimum temperature region, 1000 C < T < 1100 C. Both calcination and sulphation can be fast, being virtually complete in less than 600ms. The apparent speed of both the calcination and sulphation reactions inside the narrow temperature range suggests that sorbent injection in the upper furnace zone, at a position where the temperature is about 1100 C would perhaps be the most favourable injection position. However, if this is to be successful, good and fast mixing between the sorbent and combustion products must also be achieved.

5. CONCLUSIONS

- With a CaCO3 based sorbent the calcination rate was strongly dependent on temperature. In order to achieve a 50% calcination level of about 50ms was required at 1100 C, 80ms at 1000 C and 250ms at 900 C. Above 1200 C the calcination rate was extremely fast.

- With a Ca(OH)2 sorbent, calcination was virtually complete in about 50ms for temperatures ranging from 700-1300 C, but CaCO3 was found to form quickly to an amount in correspondence with thermodynamic equilibrium; almost 60% at 700 C, 25% at 900 C and 15% at 1100 C. When SO2 was present there appeared to be a competition between CaO combination with CO2 to form CaCO3 or with sulphur to form CaSO3 or CaSO4.

- The bench scale tests have thus far shown that sulphation is also a relatively fast reaction when the gas temperature is between 1000 C and 1100 C approaching an asymtotic value after about 500-600ms. Calcium utilization values of at least 20% for CaCO3 and 35% for Ca(OH)2 appear obtainable under the correct temperature conditions and gas environments within this residence time. Work is continuing to determine better the utilization level potentially obtainable for different type carbonate, hydroxide and dolomite sorbents.

- When burner and furnace conditions were such to give a peak flame temperature of only 1250 C or when the sorbent was injected in an air stream outside the flame, calcium utilization figures of greater than 25% for $CaCO_3$ and 35%-40% for $Ca(OH)_2$ have been achieved in 2.5MW pilot plant scale tests.

- Due to the high temperatures expected in large bituminous coal boilers and the complex mixing between burner rows and the fast potential calcination and sulphation rate at temperatures between 1000 C and 1100 C, sorbent injection in the upper furnace zone in a large boiler appears to be favourable.

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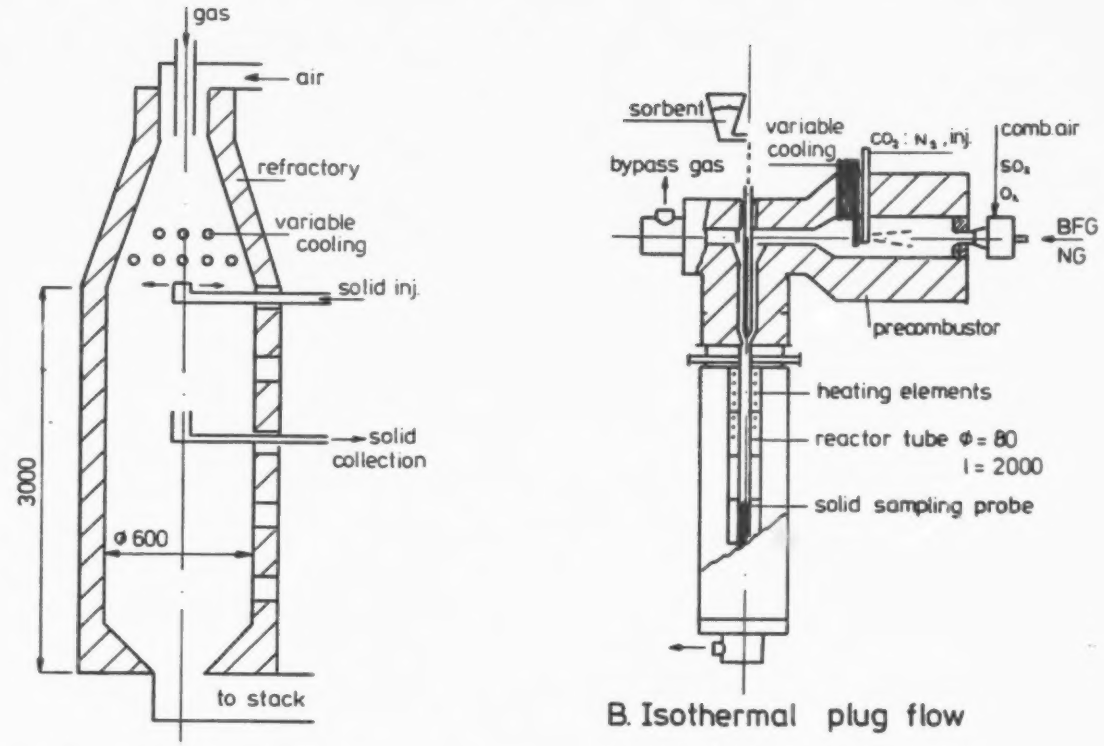
Reihe 3, Nr. 22, Oktober 1967, Forschr. Ber, VDI-Z

[7] J D HATFIELD, Y K KIM, R C MULLINS and G H McCLAELLEN
Investigaton of the reactivities of limestone to remove sulphur dioxide from flue gas
T.V.A. Report Division of Chemical Development

Fuel type		Saar	Gardanne washed	Heavy fuel oil	Delayed Coke
Proximate analysis	H_2O %	1.6	-	-	-
	Volatile %dry	31.95	44.0	-	9.1
	Ash %dry	7.9	8.4	-	-
	LCV MJ/kg dry	29.5	27.9	39.6	34.6
Ultimate analysis	Total C % dry	73.88	71.13	85.5	89.4
	O	10.97	8.55	-	1.79
	N	1.64	1.70	0.61	1.46
	H	4.72	4.85	10.27	3.34
	S	0.90	5.34	3.41	3.38
Ash composition % of total ash	CaO	8.51	20.45	-	-
	SiO_2	40.29	22.10	-	-
	Al_2O_3	22.04	12.5	-	-
	Fe_2O_3	15.38	14.95	-	-
	MgO	2.49	3.20	-	-
	TiO_2	1.06	0.60	-	-
	Na_2O	0.48	0.40	-	-
	K_2O	1.87	0.70	-	-
	P_2O_5	-	2.24	-	-
	SO_3	7.25	22.45	-	-

Sorbent type	$Ca(OH)_2$-2	$CaCO_3$ 1	$CaCO_3$ 2	Shale
Combustibles % dry	-	-	-	7.2
CaO %wt.	73.91	55.03	53.2	48.6
MgO	0.47	0.48	1.0	1.75
SiO_2	0.65	0.56	2.0	1.65
Al_2O_3	0.34	0.15	0.1	0.95
Fe_2O_3	0.13	0.09	0.3	2.0
Mn_3O_4	0.03	0.03	-	0.13
Na_2O	-	-	-	0.45
K_2O	-	-	-	0.1
TiO_2	-	-	-	0.1
P_2O_5	-	-	-	0.16
SO_3	0.04	-	-	5.1
CO_2	0.81	43.64	43.2	39.0
H_2O	23.18	-	-	-
Density kg/l	0.360	1.02	0.8	-
Specific area BET M2/g	13-32	3.52	-	-

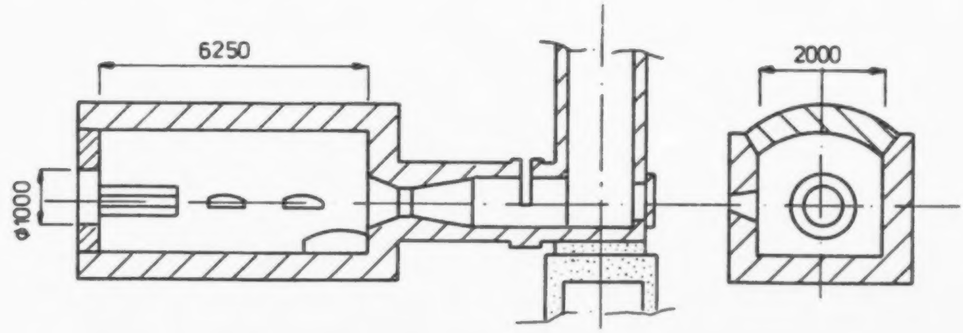
TABLE 1 - FUEL AND SORBENT ANALYSES


gas
air
refractory
variable
cooling
solid inj.
solid
collection
3000
ø 600
to stack
sorbent
variable
cooling
$CO_2 : N_2$, inj.
comb.air
SO_2
O_2
bypass gas
BFG
NG
precombustor
heating elements
reactor tube Φ = 80
l = 2000
solid sampling probe

A. Non-isothermal plug flow reactor

B. Isothermal plug flow reactor

(all dimensions in mm)


6250
ø1000
2000

C. Pilot scale test furnace

Fig. 1. Experimental facilities used during sorbent injection trails.

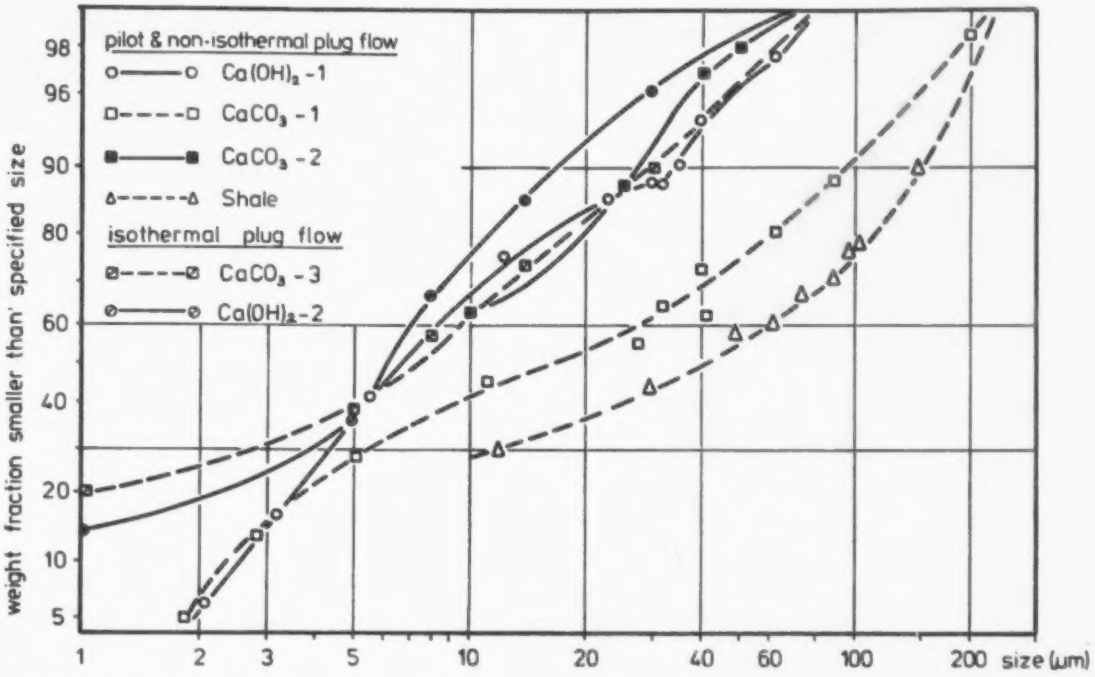


Fig. 3. Particle size distribution of various sorbents

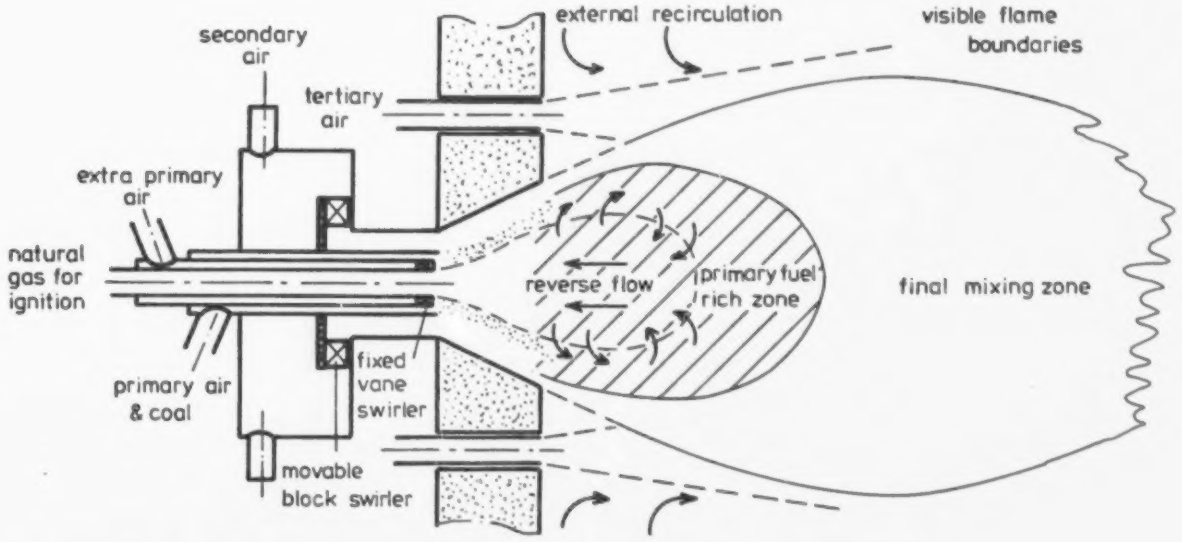

secondary air
tertiary air
extra primary air
natural gas for ignition
primary air & coal
fixed vane swirler
movable block swirler
external recirculation
visible flame boundaries
reverse flow
primary fuel rich zone
final mixing zone

Fig. 2. Schematic and principle of the experimental staged mixing burner for low NO_x combustion of pulverized coal.

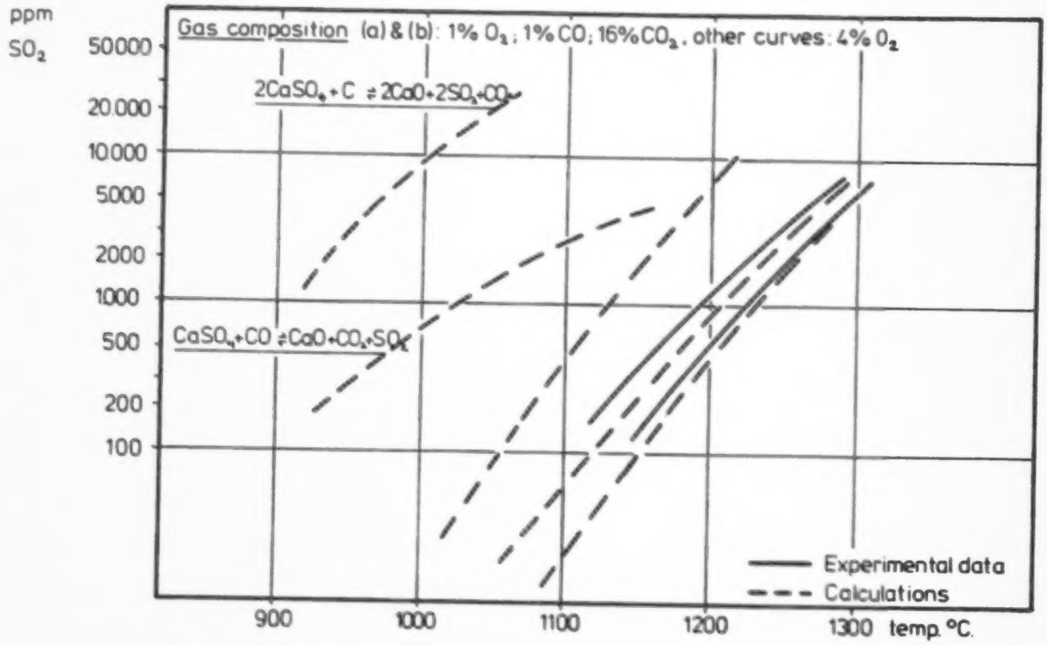


Fig:5. Thermal stability of $CaSO_4$; Experimental and theoretical data from literature.

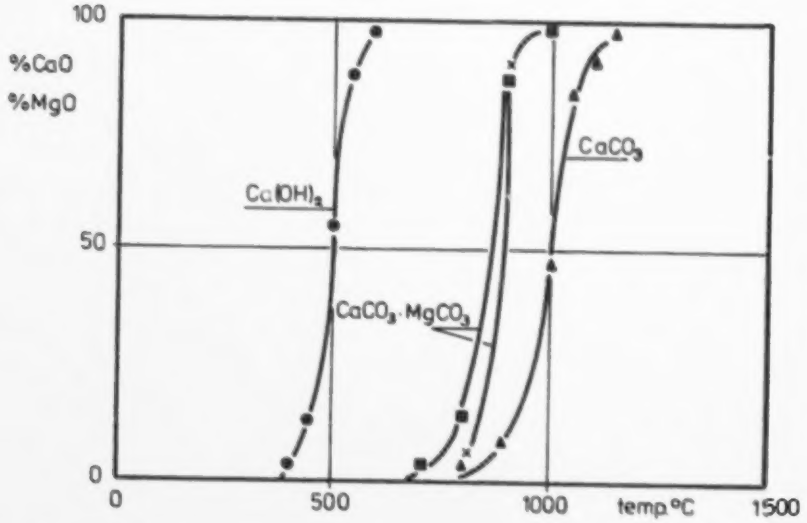


Fig: 4. Calcination characteristics of various additives

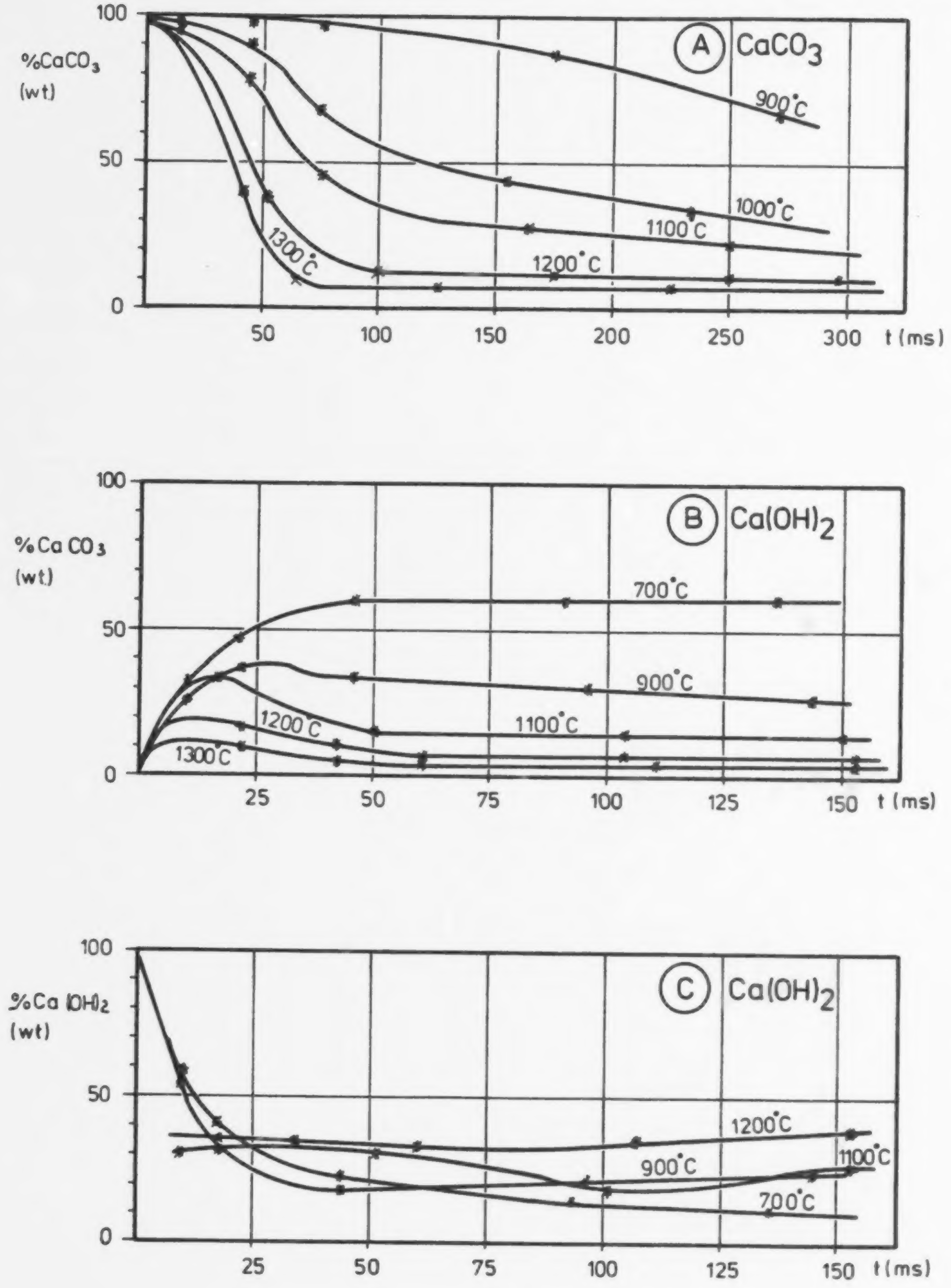


Fig:6. Calcinations results;

A. $CaCO_3$ Sorbent

B. Reformation of $CaCO_3$ with $Ca(OH)_2$ Sorbent.

C. $Ca(OH)_2$ Sorbent

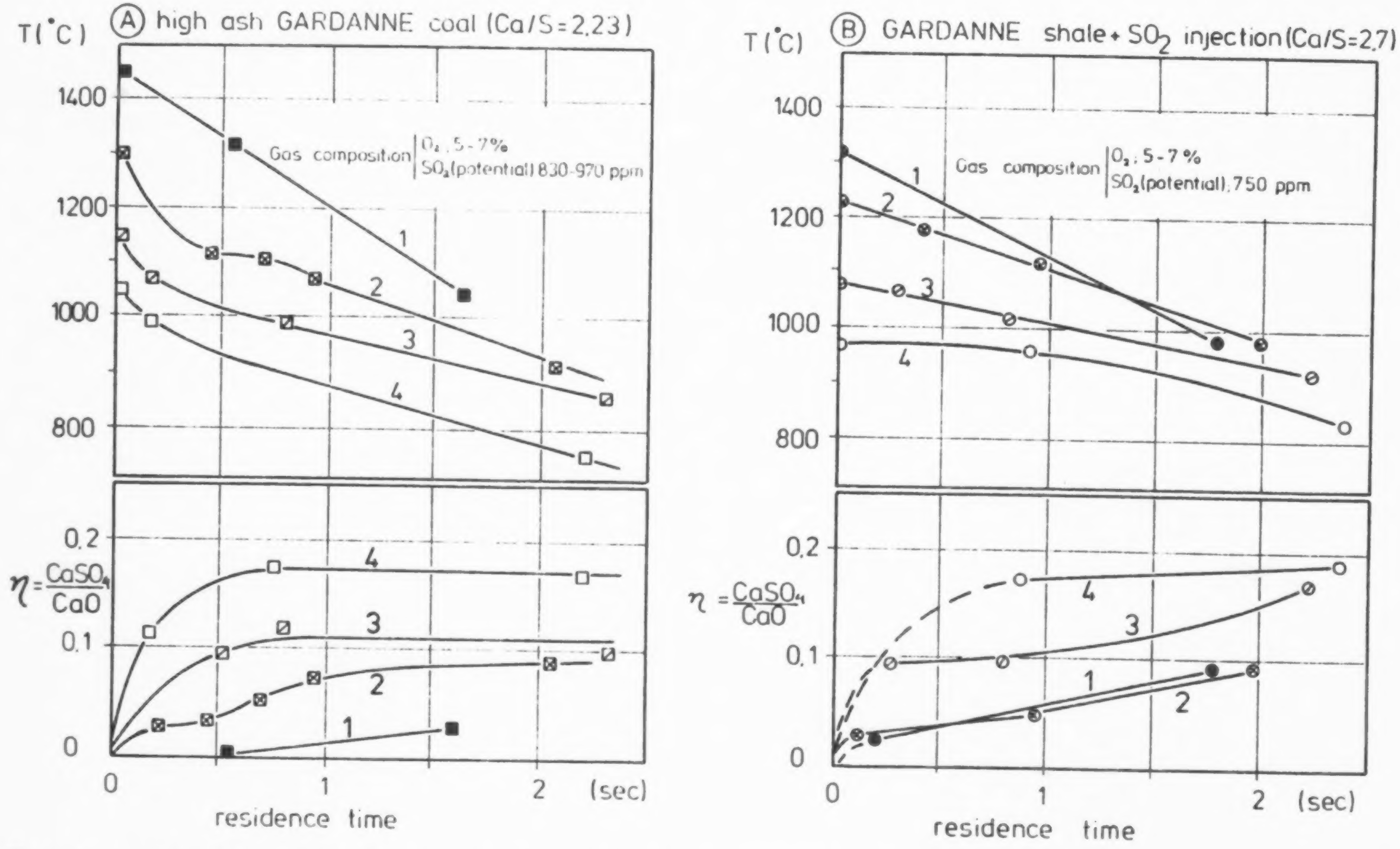
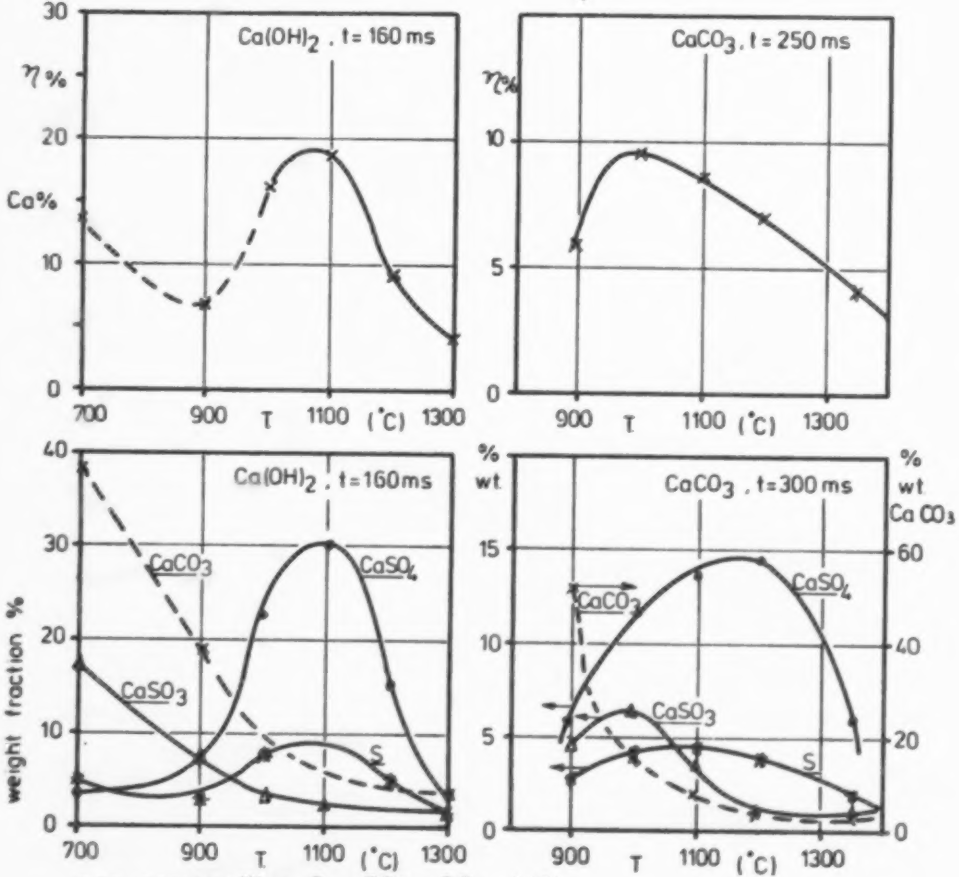


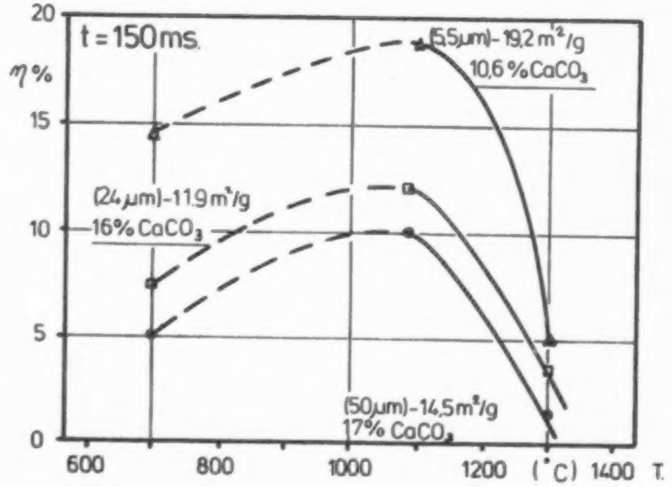
Fig: 7. Gas temperature and calcium sulphate formation in the non-isothermal plug flow furnace with shale and high ash coal from GARDANNE



gas composition; O_2-5% , CO_2-14% ,
H_2O-9.5 , SO_2-2000ppm.

Ca/S =1.7-2.1

Fig: 8. Initial sulphation results from the isothermal reactor



gas composition; O_2-5% , CO_2-14% ,
H_2O-9.5%, SO_2-2000ppm.
Ca/S= 2

Fig:9. Effect of particle size, $Ca(OH)_2$ on sulphation at various temperatures.

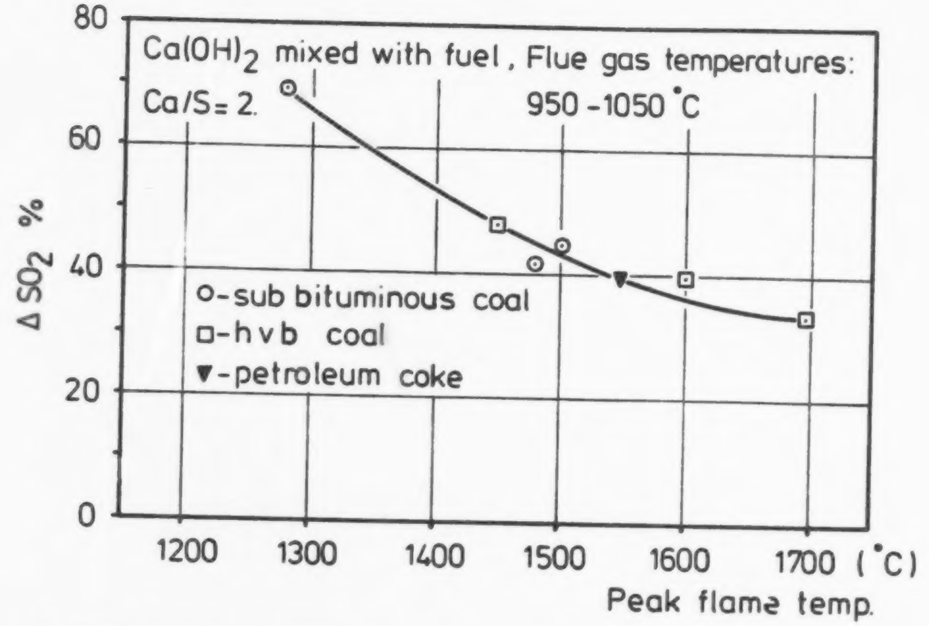


Fig:10. Effect of Peak flame temperature on sulphur capture (sorbent mixed with coal).

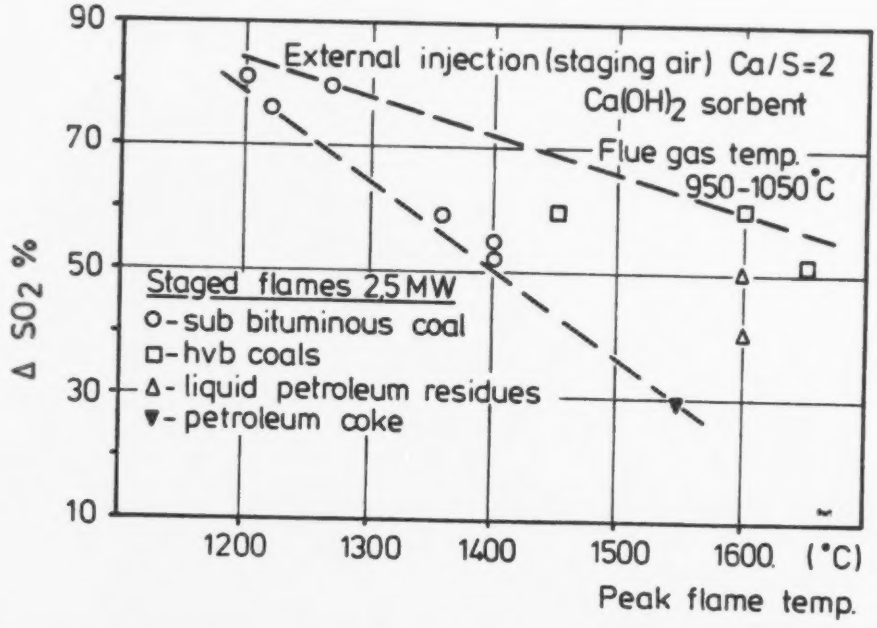


Fig: 11. Effect of Peak flame temperature on sulphur capture (external injection)

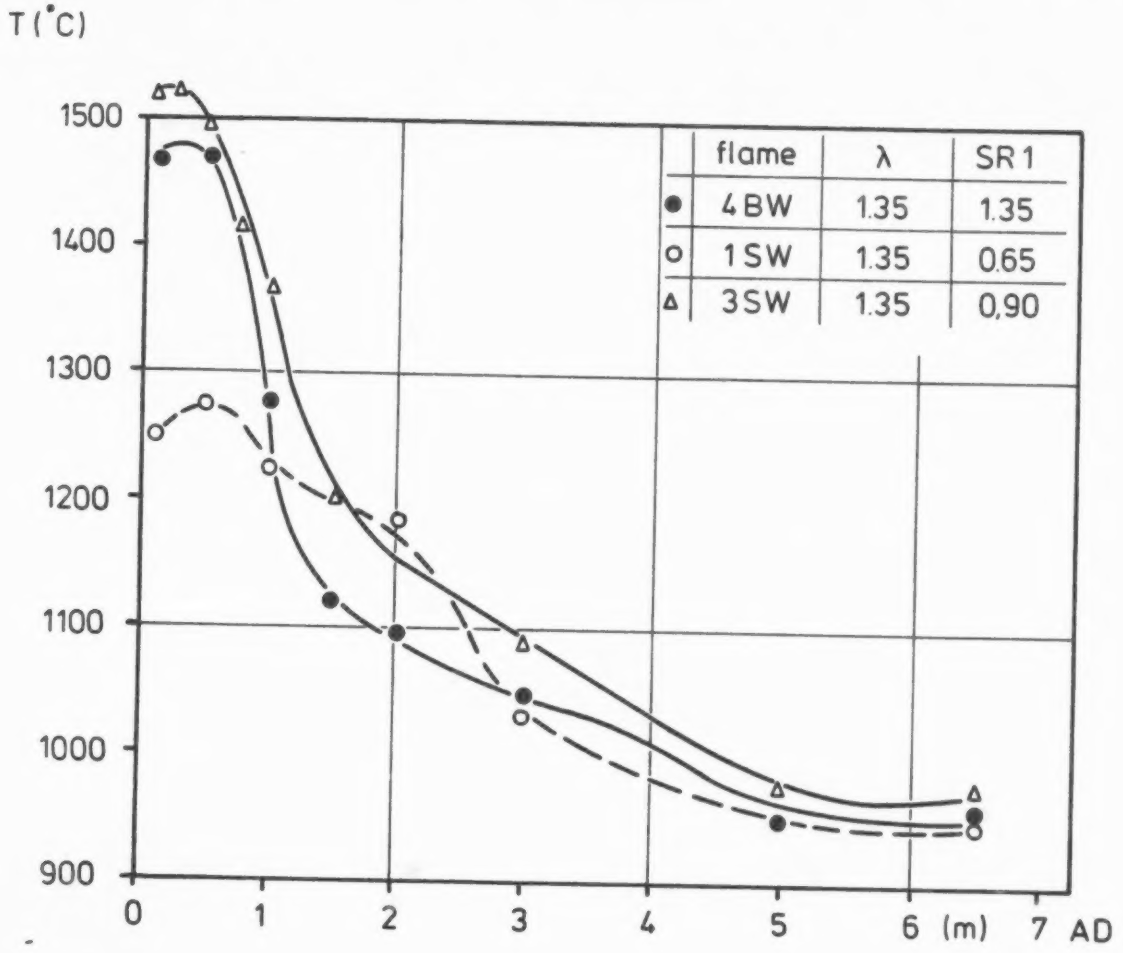
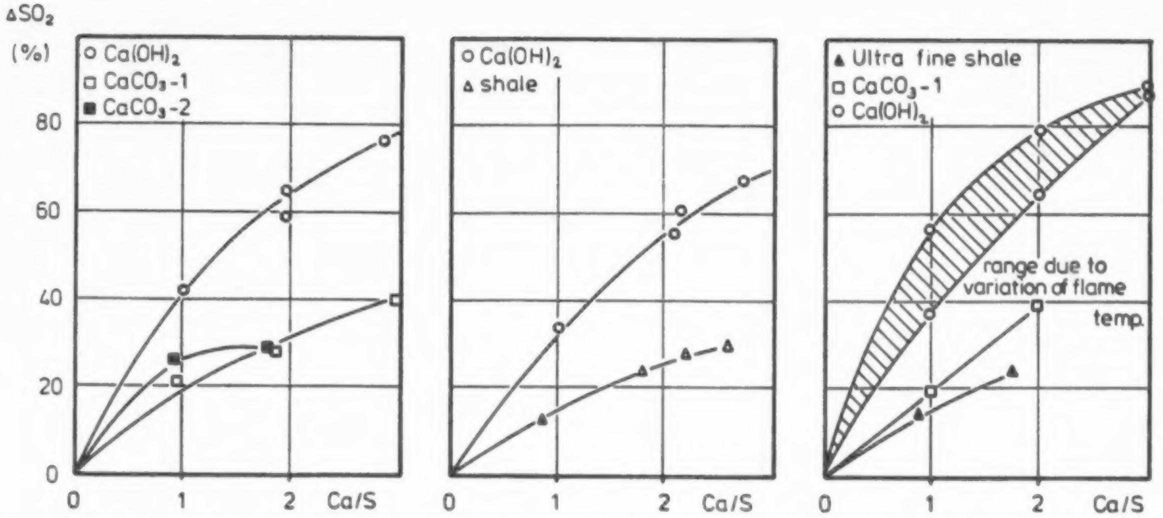


Fig: 12. On axis gas temperature along the furnace length.



Ⓐ Saar coal (1% S d.a.f) staged combustion (SR1=0,5) sorbent injected with tertiary air.

Ⓑ Gardanne washed coal (5,8% S d.a.f.) non staged combustion (SR1=1.35) sorbents injected at burner periphery

Ⓒ Gardanne washed coal staged combustion (SR1=0,5) sorbent injected with tertiary air.

Fig:14. Effect of sorbent type and mass flow on SO_2 capture for various flames with Saar coal and Gardanne coal.

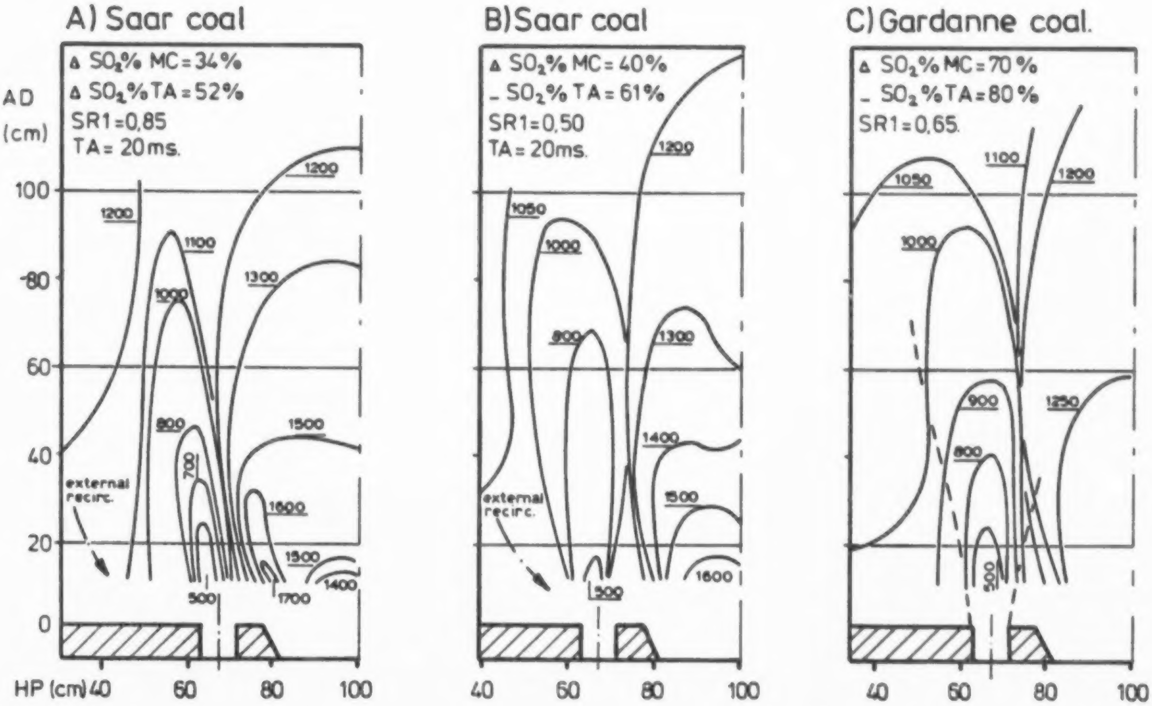


Fig:13. Staged flames, flame temp. and SO_2 removal rates with $Ca(OH)_2$ injection (Ca/S = 2)

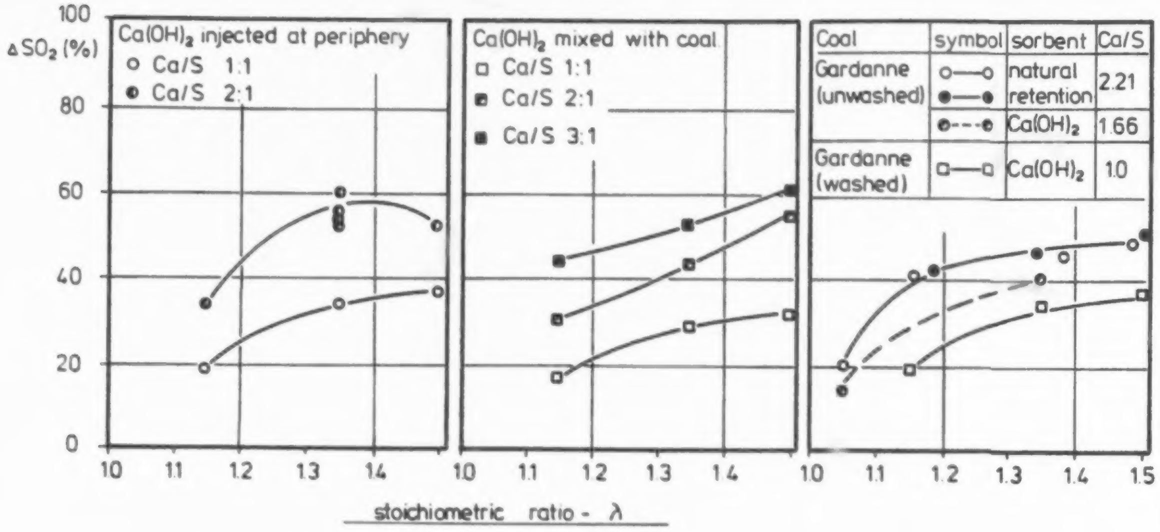


Fig:16. Effect of excess air on sulphur capture efficiency

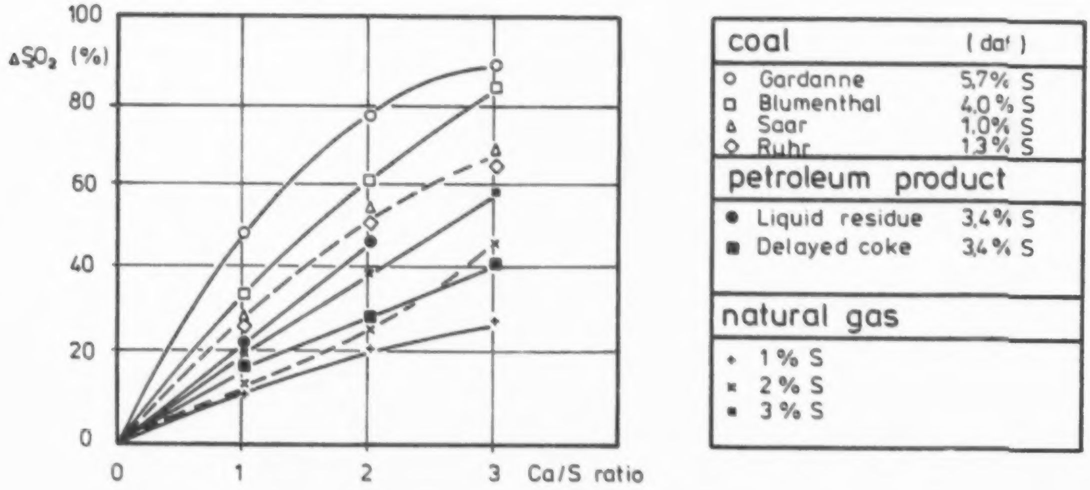


Fig:15. Effect of fuel type on sulphur capture ($Ca(OH)_2$ external injection.)

DEMONSTRATION OF BOILER LIMESTONE INJECTION IN AN INDUSTRIAL BOILER

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ABSTRACT

Consolidation Coal Company (Consol), through its Research & Development arm, Conoco Coal Research Division, made a commitment to expedite the development of Boiler Limestone Injection technology (BLI) via demonstration in a Du Pont boiler (110,000 lb/hr of steam) during the summer and fall of 1984. The goal of the program was to demonstrate the technical and economic viability of both LIMB and LI (injection above the burner zone) as low cost retrofit SO_2 control technologies, while burning a Consol Northern West Virginia high-sulfur coal. Technical objectives included SO_2 removal capability with fifty percent as a minimum target, boiler operability issues, and ESP impacts. Commercial low-NO_x burners purchased from Foster Wheeler Energy Corporation were used in the LIMB testing. Research-Cottrell supplied an electrostatic precipitator and humidification system. The demonstration program, test equipment, preliminary results, and BLI economics are described.

INTRODUCTION

With the passage of the 1971 Clean Air Act, stringent environmental regulations were applied to existing boilers through State Implementation Plans. Additionally, the current debate concerning federal "acid rain" control further indicates the need for a low cost, retrofit sulfur dioxide (SO_2) control technology. In the case of New York State, an acid rain bill was passed into law.

Conoco Coal Research Division (Conoco) is committed to evaluate, develop, demonstrate, and/or commercialize cost effective SO_2 compliance technologies. The strategy is to create a suite of retrofit SO_2 abatement technologies because no one process will be the panacea for all coal users. Site-specific economics dictate appropriate SO_2 control strategy for each coal application. Boiler Limestone Injection (BLI) is emerging as one potentially cost effective approach to SO_2 control for high-sulfur coal applications.

In 1982, Conoco conducted a detailed review and economic comparison of retrofit SO_2 control technologies which included wet limestone/lime FGD, spray dryer FGD, coal cleaning, and BLI. Conoco concluded BLI had potentially attractive economics for cases requiring up to 50% SO_2 removal, but major technical uncertainties existed for applications to U.S. coals and to U.S. boilers. The most critical issues were SO_2 removal capability in a large utility boiler and possible boiler operability problems including derate of generation capacity or significant loss in boiler efficiency. Furthermore, the impact on ESP performance could dictate additional particulate removal equipment at a cost which could eliminate any potential economic driving force for BLI. (An economic comparison of BLI to conventional FGD is described later in this paper.)

The simplicity and the potential low capital costs of BLI were sufficiently attractive for Conoco to commit to a development and demonstration program specifically designed for the application of BLI to Consol coals. The overall goal is to expedite the commercialization path of BLI.

The first phase of the program involved BLI screening tests in the Conoco 1.5 MM Btu/hour pilot-scale combustor located at Library, Pennsylvania. The objectives of these tests were to determine practical ranges of SO_2 removal as well as identify any major radiant-section slagging or convection pass solids build-up (fouling) problems. A Consol Northern West Virginia coal containing about 2.5% sulfur, 6.5% ash, and 13,800 Btu/lb was the main coal tested. The results were:

- Achieved up to 70% SO_2 removal at a limestone based Ca/S molar ratio of 3.0,
- Observed no signs of harmful slagging or fouling deposits, and
- Quantified the strong residence time/temperature relationship for SO_2 removal.

This work was supported by extensive Conoco laboratory efforts to better understand the chemistry of limestone injection. (The details of the pilot-scale combustor results will be presented at the SME/AIME Conference in New York in February, 1985.)

With these encouraging results, Consol agreed to support a BLI demonstration at the Du Pont Martinsville, Virginia plant. The goal was to establish technical and economic viability of both limestone injection integral with multistage burners (LIMB) and limestone injection into other locations in the boiler (LI). The term "LIMB" is used in this paper to generally describe injection integral with the burners although LIMB originally described a specific method of limestone injection using the EPA Distributed Mixing Burner.

DEMONSTRATION EQUIPMENT

A simplified schematic of the BLI equipment layout at Martinsville is shown in Figure 1. The system consists of limestone handling, limestone injection, particulate collection, and solids disposal.

Limestone Handling

The limestone handling system was designed by Conoco Process Engineering. Pulverized limestone (>70% minus 200 mesh) was delivered by trucks and pneumatically transferred into the limestone storage bin. The storage bin capacity was 45 tons. (In a commercial operation, it will normally be more cost effective to pulverize on-site rather than purchase pre-pulverized limestone.)

The limestone was purchased locally on a specification of ≥90% $CaCO_3$ and less than 5% $MgCO_3$. Final selection was based on SO_2 removal capability as measured in the Conoco pilot-scale combustor and limestone surface areas as determined in the Conoco laboratory.

Two gravimetric feeders conveyed the limestone from the storage bin to the pneumatic transfer system. Each feeder operated independently and could feed from 0 to 4000 pph of limestone (equivalent to a Ca/S ratio of 4.0). The limestone from each of the gravimetric screw feeders passed through a rotary valve into a 4-inch diameter transfer pipe. The transfer lines were both equipped with a positive displacement, lobe-type air blower. The blowers were designed to maintain a pick-up velocity of 60 to 75 ft/sec.

The limestone was pneumatically conveyed about 300 feet through two 4-inch lines from the limestone handling area to the boiler. The limestone was then split to the various burner injection and LI configurations by a series of splitters.

The limestone handling system was simple to start and shut down. The limestone addition rate was controlled by setting the desired Ca/S ratio using the Du Pont powerhouse computer control system. The set point for the limestone gravimetric feeders was then automatically changed based on the boiler steam load.

Limestone Injection

The host boiler was a pulverized coal, wall-fired, 3-steam drum, Sterling-type boiler built in 1941 by Combustion Engineering. The boiler rating was 110,000 lb/hr steam at 545 psi and 720°F (15 MW electrical equivalent assuming a 10,000 Btu/kWh heat rate). A schematic of the boiler is shown in Figure 2. The boiler was equipped with steam soot blowers for the superheater and boiler tubes. Since the radiant section had no soot blowers, it was necessary to hand lance the screen tubes and the radiant section tubes with 100 psig air. For a permanent BLI installation, additional soot blowers would have been installed for these tubes as well.

Although the Du Pont boiler did not have a conventional "nose," a reheat section, or a Lungstrum regenerative air heater as in a typical utility boiler; the tube spacings in the convection pass were as tight or tighter than most utility boilers (Table 1). Consequently, the effect of additional solids loading on the heat transfer sections gave a good indication of utility boiler operation. Moreover, since the radiant section temperature profiles of this boiler were representative of many utility boilers as indicated by the full-load furnace gas exit temperature of 2100°F, SO_2 removal capability should simulate performance in a larger boiler.

The only coal tested during the BLI demonstration was the same Consol coal tested in the Conoco pilot-scale combustor program, i.e., 2.5 ±0.3% sulfur, 6.5% ash, and 13,800 Btu/lb as-burned.

Both LIMB and LI SO_2 removal techniques were evaluated during the demonstration program. For LIMB, four new multistage low-NO_x burners were installed during an annual boiler turnaround in April and May of 1984. The new burners were purchased from Foster Wheeler Energy Corporation and were the commercially available Controlled Flow/Split-Flame model.[1] Each burner had a nominal heat release rating of 40 MM Btu/hr. Burners for utility installations would be almost identical in design but 100 to 300 MM Btu/hr capacity.

Boiler performance with the test coal was evaluated during a coal-alone baseline run in October of 1983 with the old burners. The new burners were tested with and without limestone addition in June through September, 1984. Foster Wheeler assisted Conoco during the baseline and LIMB portions of the testing program.

In the limestone injection (LI) mode, limestone was injected into the boiler at three different elevations on the wall opposite of the burners and on the side walls (Figure 2). The different elevations represented different gas temperature regions and different residence times. During the LI portion of the testing program (in progress at this time), a parametric test matrix included the following variables: injection elevation, number of injectors (maximum of six), injection depth, injection velocity, and injector tip design. The effects of gas temperature at the injection location, residence time, and limestone distribution were a function of these independent variables.

The LI approach is an alternative to LIMB, especially for boilers where the burner heat release rate is sufficiently high that the resulting furnace gas temperatures exceed the gas temperature application limitations of burner injection, i.e., a furnace gas exit temperature greater than 2300°F. The application of LI is boiler specific, and the following two points must be addressed:

1. Is there sufficient residence time available in the optimum - temperature window for SO_2 capture at cost effective limestone utilizations?

2. Can a LI system be designed for limestone distribution which results in intimate mixing with the flue gas in a particular utility boiler?

These issues should be further clarified when the Martinsville data are fully analyzed and engineering judgement applied to the limestone distribution issue.

Particulate Collection

As shown in Figure 1, a 3000 to 5000 ACFM slipstream portion of the boiler flue gas was diverted after the induced draft (I.D.) fan to a pilot-scale electrostatic precipitator (ESP). Normally, the flue gas from the boiler goes to a baghouse which is common for all Martinsville boilers. The ESP system was added because most utility coal users have ESP's rather than baghouses. The ESP was supplied by Research-Cottrell, a leading manufacturer of particulate control equipment. The ESP consisted of two fields which yielded a total equivalent 216 SCA at 4000 ACFM. The plate and wire configuration was typical of pre-1971 installations designed for high-sulfur coal applications.

With the addition of limestone, which is converted to lime and calcium sulfate in the boiler, the ESP inlet particulate grain loading increases substantially along with the resistivity of the particulates. Both aspects have a negative impact on the ESP performance because of its constant efficiency characteristic and its natural dependence on electrical properties of the particulates. ESP emissions could increase by a factor of ten or more.

For our testing program, Research-Cottrell supplied a humidifier as a means to compensate for both the increased loading and resistivity effects. The humidification or evaporative cooling approach had three benefits:[2]

1. Cooling of the flue gas resulted in lower gas volume which means a higher effective SCA for the precipitator.

2. Cooling of the flue gas allowed enhanced electrical energization of the ESP.

3. Cooling and humidification reduced particulate resistivity as observed in dry scrubbing applications.[3]

Pulsed energization[4] was also studied to address the high resistivity problem associated with BLI. Since pulsed energization does not compensate for the increased particulate loading, it must be used in combination with humidification or some other means of flue gas conditioning to obtain coal-alone base level emissions.

Solids Disposal

The Martinsville plant used a water-hydrovac system for both fly ash and bottom ash. The Du Pont hydrovac ash removal system was modified to alleviate the problems experienced during the TVA Shawnee limestone injection test in the early 1970's.[5] When the lime modified fly ash is exposed to water, it has pozzolonic or cement-like properties. A pneumatically driven ram device was installed in the hydrovac inlet piping to clear any solids build-up in the hydrovac throat. The number and diameter of the hydrovac water nozzles were also increased to provide increased conveying capacity.

The limestone/lime/calcium sulfate/coal ash slurries from the bottom ash, ESP, and baghouse were then sluiced to a settling/surge Hypalon®-lined pond which was constructed for these tests. The pond had sufficient residence time (minimum of 8 hours) to settle the solids. The supernate from this pond had a pH of greater than 11 and required neutralization with concentrated sulfuric acid to comply with plant effluent pH specifications. The neutralized overflow was then channeled to the existing main ash pond.

The high cost involved with ponding and neutralization would normally dictate dry solids disposal for large-scale, long-term operation. For these tests, site-specific requirements made the ponding/neutralization approach more economical.

PROGRAM OBJECTIVES

The technical objectives of the demonstration program covered SO_2 removal capability, boiler operability issues, and ESP impacts.

SO_2 removal capability was studied over the operating range of the boiler within reasonable limestone addition rates as dictated by economic constraints. Fifty percent SO_2 removal was the target for both LIMB and LI. Operating range of the boiler included fifty percent load to full load. Testing was limited to a maximum limestone addition rate equivalent to a 3.5 Ca/S molar ratio. The use of four burners (two rows of two burners each) permitted the study of burner-to-burner interaction on SO_2 removal capability which had not been fully addressed on pilot-scale combustor units.

Boiler operability issues such as potential derate or substantial loss in boiler efficiency were major concerns going into the demonstration program. For every four to five tons of high-sulfur coal burned in a boiler, about one ton of limestone is required for 50% SO_2 removal. A big question mark with BLI was "how would these additional solids affect the heat transfer surface areas in the radiant and convection pass sections?"

The impact on ESP performance and the effectiveness of particulate emission mitigation techniques are critical to the process economics of BLI. The addition of a new ESP or baghouse could double the capital cost requirements of BLI.[6]

PRELIMINARY RESULTS

Since the demonstration program is still ongoing at this time, only preliminary data and conclusions are presented here. Further reduction of the data is required before detailed analysis can be reported. Full material balances will be presented in a future paper.

LIMB Testing

Baseline boiler testing on the high-sulfur Consol coal without limestone addition was performed with the new burners during June and July, 1984. During this period, the burners were tuned for optimum low-NO_x and burner flame conditions. A NO_x level of 0.4 lb/MM Btu was achieved and subsequently maintained throughout the LIMB testing program.[7]

LIMB testing began in mid-August and was completed at the end of September. Testing was around-the-clock on a seven-days-a-week basis. The testing was made in two phases: screening/optimization tests and longer term tests.

a. SO_2 Reduction

After several weeks of screening and optimization tests, 50% SO_2 reduction was demonstrated at a Ca/S molar ratio of 2.5 to 2.75 during a three-day run. Equivalent calcium utilization was about 18% to 20%. During the LIMB screening and optimization tests, best calcium utilization resulted while injecting limestone into only the top two burners. This mode of injection was then used during the long-term runs.

SO_2 reduction (measured by SO_2 analyzer and modified EPA Method 5) was a strong function of Ca/S ratio and boiler temperatures, which vary both with boiler steam load and cleanliness of the boiler.

SO_2 removal data were collected between Ca/S ratios of 1.5 and 3.5. The calcium utilization decreased slightly as the Ca/S ratio was increased in agreement with work by others.[8,9,10] An exact correlation was difficult to determine because of the background interference caused by the change in load and the cleanliness of the boiler as measured by the solids build-up rate on the heat transfer surface areas. For example, as boiler load was decreased from 110,000 lb/hr to 50,000 lb/hr (half load), SO_2 reduction increased to over 60% at a Ca/S ratio of 2.5.

The impact of boiler cleanliness on SO_2 removal is illustrated in Figures 3 and 4. In Figure 3, SO_2 reduction is plotted versus time. With clean tubes at time zero, SO_2 removal was 55%. As illustrated in Figure 4, as the heat transfer surface areas were covered with deposits, the flue gas temperature increased. The boiler gas exit temperature increased until after four hours soot blowing was required as dictated by the steam superheat temperature alarm point. With these higher boiler gas temperatures, SO_2 removal dropped off to about 50%. When soot blowing and hand lancing were not performed for a 14-hour period, as shown in Figure 3, SO_2 removal dropped off to 42%.

b. Boiler Operability

The addition of limestone did not cause any boiler derate as 110,000 lbs/hr steam was achievable while removing 50% SO_2. Also, no significant loss in boiler efficiency was measured during these conditions.

With the addition of limestone, the inert solids loading in the boiler increased by a factor of about three compared to coal-alone baseline tests. (At full boiler load, about 2200 lb/hr of limestone was required to achieve 50% SO_2 removal.) Based on visual observations, the solids deposition rate on the radiant and screen tube sections of the boiler also increased by a factor of three when limestone was added at a 2.5 Ca/S ratio. The tube deposits were very friable and easily soot blown, and increased boiler cleaning frequency maintained steam cycle and boiler exit temperatures within control limits as illustrated in Figure 4. Comparisons of frequency of convection pass soot blowing and boiler hand lancing plus ash pulling duration are shown in Table 2 for operation with and without limestone addition. The radiant section of the boiler required the most dramatic impact in cleaning cycles, which increased from once per day to four times per day.

LI

Limestone injection testing began on October 1 and was limited to a 30-day testing period. Preliminary results supported the earlier pilot-scale observations that SO_2 removal is a strong function of injection location and injection methods. About 50% SO_2 removal was achieved at a Ca/S ratio of 2.5 while operating at about 80% of full boiler load. For the Martinsville boiler, preliminary data also indicated that calcium utilization was slightly lower during best LI conditions compared to LIMB operation. Further testing is in progress to determine if either residence time and/or limestone distribution is the cause for the difference in results.

Boiler operability impacts appear to be less with LI operation compared to LIMB operation because of a reduced solids deposition rate in the boiler radiant section. Other impacts are similar to LIMB operation.

Boiler Inspection

After two months of semi-continuous limestone addition, the boiler was shut down in mid-October and thoroughly inspected for any erosion, corrosion, or pluggage. No unusual solids deposits, corrosion or erosion were found. Even though no catastrophic short-term effects were evident, a much longer period of operation, i.e., six months to one year, is required to demonstrate lack of problems in a utility boiler.

Particulate Collection

The additional lime and calcium sulfate material from the test boiler presented no problems to the Martinsville baghouse. Some plugging problems were experienced, however, when the lime-modified fly ash from the baghouse ash hoppers was inadvertently wetted and allowed to deposit in the ash removal piping. Other plugging problems were experienced in the vacuum side of the hydrovac system indicating that additional conveying capacity may be required.

As previously discussed, limestone addition creates problems with ESP operation, and mitigation control techniques are required to avoid installing costly additional ESP plate area or a new baghouse. While operating at a 2.5 Ca/S ratio, the particulate loading increased by a factor of three and the resistivity increased from a satisfactory level of 10^9Ohm-cm to a more troublesome level of $2\text{x}10^{11}$ Ohm-cm. As a result, the ESP particulate emissions increased by a factor of 8.4 when compared to operation with only the coal fly ash. This emission is approximately equivalent to burning a coal having an ash content of 37%.

The results of the pilot-scale ESP tests are summarized in Table 3. ESP performance is expressed in two ways:

1. The relative emission rate expressed as a fraction of the particulate emissions experienced during the boiler limestone injection case with the ESP alone.

2. The equivalent coal ash content which relates the emission to a hypothetical high-sulfur coal only, unaltered ESP case.

Baseline tests with coal-alone showed particulate collection efficiencies in the 98% to 99% range, levels typical for a full-scale unit.

Two potentially cost effective technologies, pulsed energization and humidification, were tested as control strategies to improve the particulate emission level. These technologies were tested independently and in conjunction with one another.

Humidification in combination with the use of low ash coal was the most effective mitigation strategy, reducing the boiler limestone injection base emissions by a factor of four (relative emissions rate of 0.24). The emissions for this case were equivalent to burning a 12% ash coal in the boiler. Further emissions reduction is expected for full-scale units where the existence of additional ESP electrical fields should reduce the impact of gas (and solids) bypassing and particle re-entrainment. For example, a six percent bypass would account for the difference in emissions between the coal-only and the BLI plus humidification cases.

Pulsed energization in combination with a low ash coal overcame the penalty resulting from high particulate resistivity improving the baseline boiler limestone injection emission by a factor of 1.7 (relative emission rate of 0.58). This emission is equivalent to feeding high-sulfur coal having an ash content of 25%.

These preliminary ESP results are based on screening tests. Longer term confirmation runs were made during the long-term LI testing program in late October.

Conoco also evaluated SO_2 reduction potential across the ESP by operating the humidification process at a closer approach to dew point than would be required for particulate removal alone. (A la spray dryer FGD.) Results are too preliminary to report at this time.

Solids Disposal

The solids wastes (lime/calcium sulfate/modified fly ash) generated during this test program were settled in the Hypalon®-lined pond as discussed previously. The solids will be covered with fly ash and landfill, and the area will be reclaimed.

The issue of solids disposal in a commercial installation must be addressed on a site-by-site basis. The preferred and probable method will be dry disposal and would be similar to handling waste solids from a FBC or spray dryer FGD system. Conoco is actively studying this area. Several drums of lime/calcium sulfate/modified fly ash were provided to the Electric Power Research Institute (EPRI), who plan to evaluate the disposal implications of BLI created wastes in 1985.

BLI ECONOMICS

Conoco has completed a 500 MW economic comparison of BLI and conventional wet lime or limestone FGD for utility retrofit applications using a 2.5% sulfur coal (Figure 5). The costs are plotted on a dollars per ton of SO_2 removal basis to compare processes which have different SO_2 removal efficiencies. Both BLI and FGD economics were determined on a consistent basis so relative costs are comparable. Absolute dollars were intentionally left off the figure to avoid debate over the assumptions and bases of economic analysis. Capital costs are represented by the crosshatched portion of the bars. O&M costs are the remaining portion.

Two bars are shown for the wet FGD approach. The main difference between the FGD bars reflects the degree of difficulty in retrofitting an FGD system into an existing power plant. The "easy" retrofit represented by the left bar would reflect ample space available and no major equipment relocation. The right bar would reflect a "difficult" retrofit installation representing a congested limited space scenario. The difference between these two cases could be a factor of two in capital costs.

The main assumptions for the BLI case were:

- 50% SO_2 removal at a Ca/S ratio of 2.5.
- No major boiler modifications required other than new burners or LI injection equipment.
- No major ESP modifications; that is, humidification plus new rappers, ESP controls, etc. are sufficient.
- Limestone at $12.50/ton delivered and waste disposal at $7.50/ton.

The main cost driving force of BLI compared to conventional scrubbing techniques is the potentially lower capital requirements. The "easy" and "difficult" FGD cases require about 70% and 220% more capital, respectively, compared to the BLI scenario. On a total cost basis, BLI is about 25% to 50% lower than the FGD cases.

As with all SO_2 abatement strategies, BLI costs are very site specific. Since limestone and disposal costs account for about 45% of the total costs, the attractiveness of BLI is a strong function of these site specific factors.

In summary, BLI looks extremely attractive compared to conventional scrubbing if a plant has a favorable limestone supply and solids disposal situation or if the plant has a difficult FGD retrofit problem. Obviously, the boiler must have a satisfactory temperature/residence time profile for BLI to be effective before these other site-specific factors can even be considered.

CONCLUSIONS

Based on the analysis of preliminary data from the boiler limestone injection demonstration at Martinsville, it is concluded:

1. 50% SO_2 removal is achieved at a Ca/S molar ratio of 2.5 to 2.75 while operating the boiler at full load. SO_2 removal increases at lower loads.
2. LIMB appears to yield slightly better limestone utilization than LI. It may be preferable in a commercial installation unless high burner heat release rates make LIMB non-practical.
3. SO_2 removal with BLI is very sensitive to radiant section temperature profiles caused by either changes in boiler load or cleanliness of the heat transfer surface areas.
4. BLI, both LIMB and LI, did not adversely impact boiler operability in terms of boiler derate or efficiency.
5. BLI did require changes in operating procedures, i.e., increased soot blowing, lancing, and ash hopper pulling duration. For a permanent installation, lancing could probably be avoided by the installation of additional soot blowers.
6. Humidification of the flue gas from BLI operations reduced the emissions from the pilot-scale ESP to an acceptably low level (equivalent to burning 12% ash coal without BLI). Lower relative emissions, approaching those corresponding to burning 6.5% ash coal without BLI, are anticipated in full scale ESPs which have more electric fields. Without mitigation techniques, BLI caused ESP particulate emissions to increase by a factor of eight, due to both the increased resistivity and the increased particulate loading.
7. Although it was successfully demonstrated that settling and neutralization could be implemented to comply with local water quality standards, dry disposal of the lime/calcium sulfate/modified fly ash is recommended because of economic considerations.
8. Projected BLI costs are attractive compared to conventional wet lime or limestone FGD if site specific limestone supply and solids disposal costs are favorable or if the FGD retrofit is difficult.

Acknowledgement

The authors express sincere gratitude to Robert Chesney and other Martinsville plant power house staff and to John De Ruyter of the Du Pont Engineering Service Division for their cooperation during the entire demonstration program.

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Figure 1

BOILER LIMESTONE INJECTION DEMO.

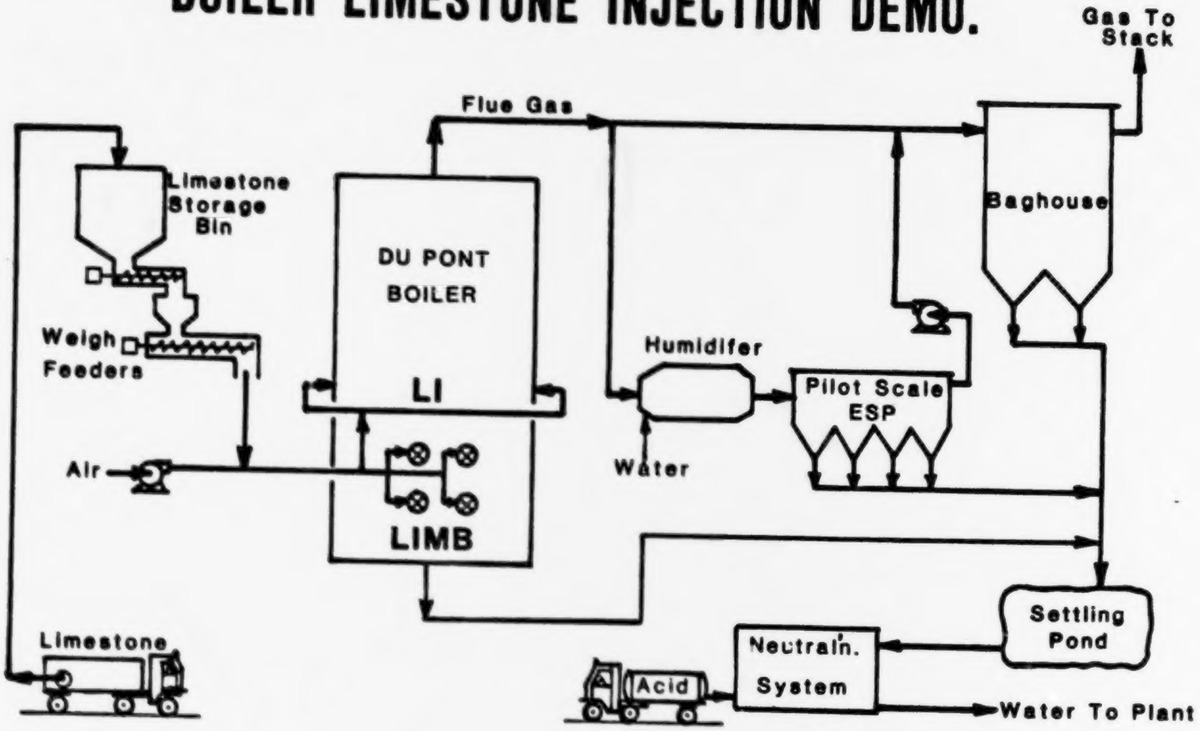
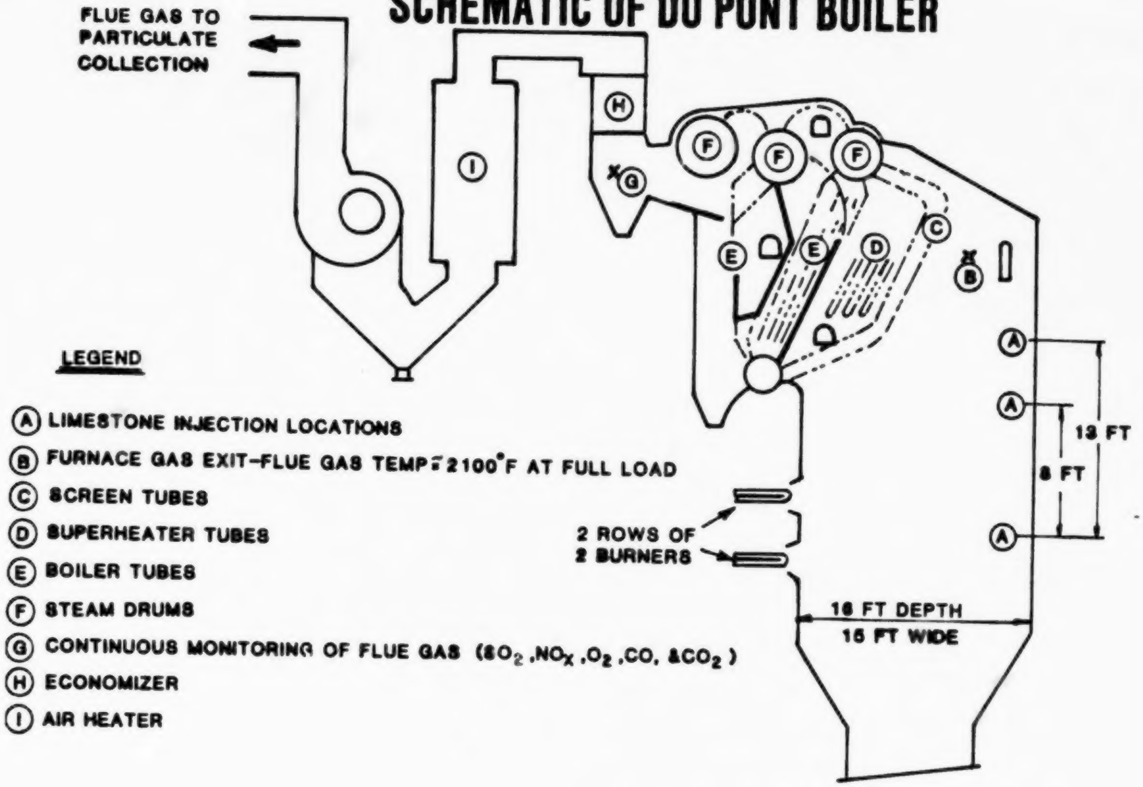

Gas To Stack
Flue Gas
Limestone Storage Bin
DU PONT BOILER
Baghouse
Weigh Feeders
Humidifer
Pilot Scale ESP
LI
Air
Water
LIMB
Settling Pond
Limestone
Neutraln. System
Acid
Water To Plant

Figure 2

SCHEMATIC OF DU PONT BOILER


FLUE GAS TO PARTICULATE COLLECTION
H
I
G
F
F
F
E
E
D
C
B
A
A
A
13 FT
8 FT
2 ROWS OF 2 BURNERS
16 FT DEPTH
15 FT WIDE

LEGEND

- Ⓐ LIMESTONE INJECTION LOCATIONS
- Ⓑ FURNACE GAS EXIT–FLUE GAS TEMP ≅ 2100°F AT FULL LOAD
- Ⓒ SCREEN TUBES
- Ⓓ SUPERHEATER TUBES
- Ⓔ BOILER TUBES
- Ⓕ STEAM DRUMS
- Ⓖ CONTINUOUS MONITORING OF FLUE GAS (SO_2, NO_x, O_2, CO, & CO_2)
- Ⓗ ECONOMIZER
- Ⓘ AIR HEATER

Figure 3

EFFECT OF BOILER CONDITIONS ON SO_2 REMOVAL

(When Soot Blowing And Hand Lancing Were Delayed)

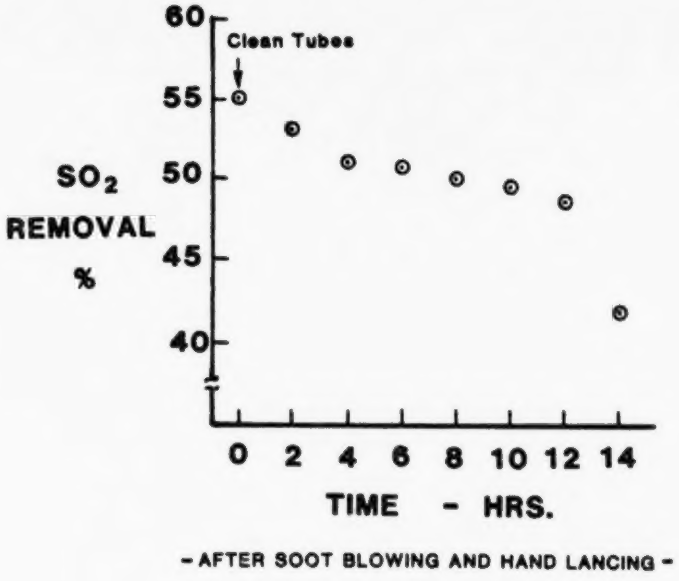


Figure 4

EFFECT OF LIMESTONE ADDITION ON STEAM AND BOILER EXIT GAS TEMPERATURE

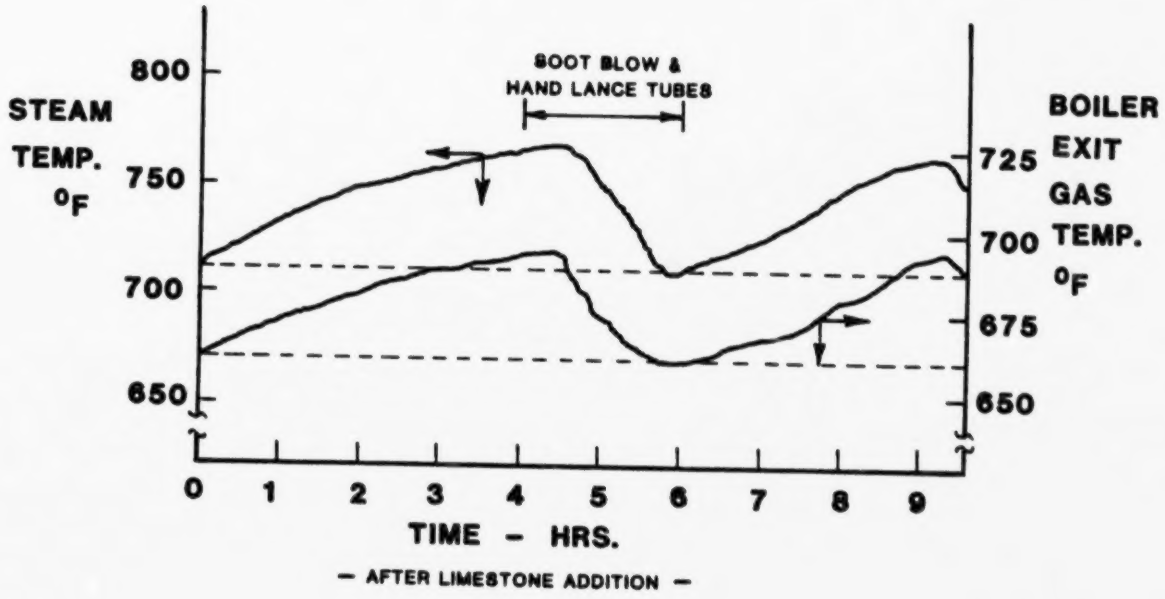


Figure 5

ECONOMIC COMPARISON OF BLI VS CONVENTIONAL WET FGD

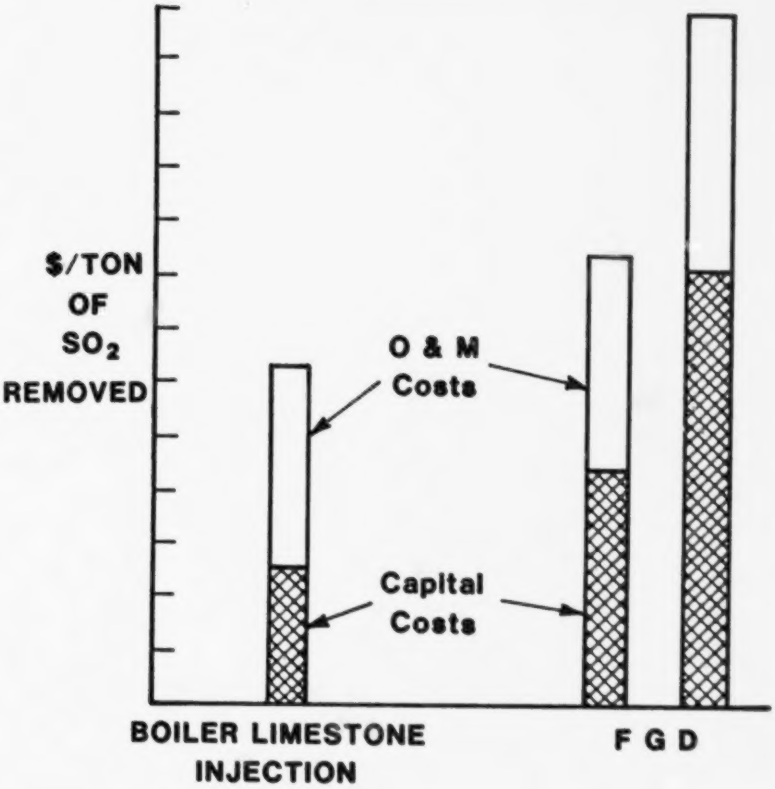


TABLE 1

DEMONSTRATION BOILER TUBE SPACINGS

BOILER TUBE BANK	CLEARANCE BETWEEN TUBES, INCHES
Screen Tubes	3.75
Superheater Tubes	1.25-2.25
Boiler Tubes	3
Economizer Tubes	1
Air Preheater	2.25 O.D.*

*Flue gas flows inside the tubes: air outside.

TABLE 2

IMPACT OF BLI ON BOILER OPERABILITY

Frequency of Soot Blowing and Radiant Wall/Screen Tubes Cleaning Cycles and Ash Hopper Pulling Duration

OPERATION	COAL-ALONE	DURING BLI
Soot Blowing Frequency	once/shift	twice/shift
Radiant Wall/Screen Tubes Lancing Frequency	once/day	four times/day
Ash Hopper Pulling Duration	base time	three times base

TABLE 3

PARTICULATE COLLECTION PERFORMANCE

TECHNOLOGY	ASH TYPE[1]	RELATIVE EMISSION RATE[2]	EQUIVALENT HIGH-SULFUR COAL ASH CONTENT (%)
ESP	Coal Alone	0.12	6.5
ESP	Coal + BLI	1.00	37
ESP + Pulsed Energization	Coal + BLI	0.58	25
ESP + Humidification	Coal + BLI	0.24	12

[1] Test coal contained 6.5% ash.
[2] Base case of 1.00 reflects ESP particulate emission level while operating with boiler limestone injection.

PILOT-SCALE STUDIES OF IN-FURNACE HYDRATED LIME INJECTION FOR FLUE GAS SO_2 EMISSION CONTROL

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ABSTRACT

Simultaneous control of SO_x/NO_x emissions, derived from the combustion of low-rank coal, is under investigation at the University of North Dakota Energy Research Center (UNDERC). Process development work has been performed on both bench-scale and pilot-scale systems. Direct furnace injection of calcium-based SO_2 sorbent materials is the SO_2 control technique under evaluation.

Furnace injection tests have focused on the direct injection of pressure-hydrated lime at flue gas temperatures ranging from 1500° to 3000°F (815° to 1650°C) followed by collection in a baghouse operated at temperatures up to 1000°F (540°C). Sorbent utilization values up to 55% at a Ca/S mole ratio of 1.0 have been observed. Eighty percent SO_2 reduction has been observed at Ca/S mole ratios of ≤ 2.0. Sorbent utilization in the baghouse has never exceeded 10% for baghouse temperatures ranging from 800° to 1000°F (425° to 540°C). Residence time and the temperature regime of the sorbent injection location appear to be the critical parameters controlling SO_2 reduction and sorbent utilization.

INTRODUCTION

Recent national attention has focused on acid rain and its potential threat to the environment. Scientific groups and individuals across the country generally agree that acid deposition problems exist, but no consensus has been reached as to the severity of the problems, the deposition mechanisms, or the appropriate remedies. Proposals range from immediate enactment of laws to reduce SO_2 and NO_x emissions from combustion sources to additional research studies of acid deposition phenomena.

The University of North Dakota Energy Research Center (UNDERC), formerly the Grand Forks Energy Technology Center (GFETC), has been conducting flue gas desulfurization (FGD) studies since the early 1970's. The first major FGD program pioneered the use of alkaline fly ash in a wet scrubber system to control SO_2 emissions from western coals. Fly ash alkali FGD studies were conducted both on a pilot-scale process development unit and a full-scale utility boiler (1,2,3). Approximately 4200-MW of western U.S. generating capacity currently employ the fly ash alkali process to reduce SO_2 emissions. A subsequent spray dryer FGD test program evaluated spray dryer/fabric filter FGD using twenty fly ashes from lignite, subbituminous, and bituminous coals in a pilot-scale system (4). Direct injection of sodium-based SO_2 sorbents into combustion systems was also investigated. Nahcolite and trona were evaluated in a pilot-scale combustion system using a fabric filter baghouse (5). Both materials were capable of retaining 80% SO_2 with overall tests results similar to those reported by Muzio, et al (6).

Pilot-scale evaluation of direct furnace injection of calcitic and dolomitic limestone and quicklime began at the former GFETC in early 1978 (7). Sulfur dioxide reduction and sorbent utilization values did not exceed 16% for the limestone injection tests. The relatively low utilization of the limestone was probably due to an inadequate time/temperature profile necessary for reaction with SO_2 and poor development of the sorbent surface area. Maximum quicklime utilization was 32% at a Ca/S ratio of ∿1.0. A DOE-sponsored field test on a 50-MW utility boiler examined direct injection of limestone into boiler flue gas and into a burner operated in a low-NO_x, staged-combustion mode (8). Limestone utilization up to about 16% and SO_2 removal up to 47% were achieved. Samples of the resulting fly ash/calcined limestone mixture were subsequently found to be reactive in a spray dryer FGD process.

Recent work at the UNDERC has focused on the development of a dry technique for simultaneous control of SO_x/NO_x emissions from low-rank coal derived flue gas. The approach combines direct furnace injection of a calcium-based sorbent with particulate collection in a baghouse. Specifically, direct furnace injection of calcitic pressure-hydrated lime and additive-enhanced calcitic pressure-hydrated lime are under evaluation for SO_2 control. Three NO_x control techniques have been or are currently under evaluation: 1) selective catalytic reduction (SCR) using a commercial NH_3/SCR reactor system installed downstream of a high-temperature baghouse (800°-1000°F, 425°-540°C), 2) collection of potential throwaway NO_x reduction catalysts in a high-temperature baghouse with upstream NH_3 injection, and 3) additive addition to calcitic pressure-hydrated lime with subsequent NO_x control occurring in a baghouse operated at conventional temperatures. This paper will focus on results from SO_2 control experiments on pilot-scale combustion systems.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Three combustion systems were used during the pilot-scale studies: a propane-fired system and two systems with natural gas- or pulverized coal-firing capabilities. The propane-fired (PF) combustor and the ash fouling (AF) combustor were both operated using the high-temperature baghouse. The particulate test combustor (PTC) system used a baghouse operated at conventional temperatures. A significant portion of the injection tests performed in the past year were conducted using calcitic pressure hydrated lime produced in a bench-scale batch pressure hydrator built and operated at the UNDERC. Equipment descriptions and general experimental procedures are presented in the following paragraphs.

Propane-Fired Combustor/High Temperature Baghouse System

The propane-fired combustor system has two operating configurations, high-temperature and low-temperature. This paper discusses only the high-temperature (PF/HTB) configuration.

The high-temperature configuration consists of: a propane-fired combustor, 5 annular heat exchangers, a 12-inch (30.5 cm) ID test section, a baghouse, and gas sampling instrumentation. Figure 1 provides a simplified diagram of the unit.

The propane-fired combustor is a water-cooled refractory-lined system. Four stainless steel coils are embedded in the 6 inch (15.2 cm) refractory walls to provide limited control of combustor outlet temperature. The cooling coils can be operated in either a parallel or series configuration. The outer shell of the combustor is 3/16 inch (0.48 cm) carbon steel. A sight port is located in the combustor transition section. Indicated combustor outlet temperature is nominally 2700°F (1480°C) at a combustion air flow rate of 130 ± 10 scfm (3.7 ± 0.3 m^3/min) and 4% oxygen in the flue gas (on a dry basis).

The baghouse is a pulse-jet fabric-filter type designed to operate at 130 scfm (3.7 m^3/min), and a temperature range of about 250° up to 1000°F (120° to 540°C). A total of 12 cage mounted bags, each 4.5 inches (11.4 cm) in diameter by 8 feet (2.44 m) in length, are hung from 2 tube sheets providing a total filter area of 113 ft^2 (10.5 m^2).

The flue gas sampling system is capable of extracting the flue gas from three locations in the system; post-combustor (SB No. 1), pre-baghouse (SB No. 2) and post-baghouse (SB No. 3). Flue gas is analyzed and data are recorded for oxygen (O_2), carbon dioxide (CO_2), sulfur dioxide (SO_2), and oxides of nitrogen (NO_x).

Ash Fouling Combustor/High-Temperature Baghouse System

The ash fouling combustor/high-temperature baghouse system combines a combustor with natural gas- or pc-firing capabilities with the high-temperature baghouse described previously. Figure 2 illustrates some basic system components. The combustion chamber is approximately 30 inches (76 cm) in diameter, 8 feet (2.44 m) high, and is refractory lined. Combustion air is preheated with an electric air heater. Preheat temperatures to the combustor normally run from 700° to 900°F (370° to 480°C) depending on coal moisture.

Utility grind (80% less than 200 mesh, (74 μm)) coal is produced in a hammer mill. The coal is then screw-fed from a hopper into the throat of a venturi section on the primary air line to the burner at a rate of about 75 lbs/hr (34 kg/hr). Numerous thermocouples and sorbent injection ports are located in the flue gas duct downstream of the combustor. A more detailed system description can be found in a previous publication (9).

Particulate Test Combustor System

The particulate test combustor system combines a combustor with natural gas- or pc-firing capabilities with a baghouse or ESP operated at conventional temperatures. This 500,000 Btu/hr (126,000 Kg-cals/hr) combustor was designed specifically to generate fly ash representative of that produced in a full-scale utility unit. The PTC is illustrated schematically in Figure 3. The combustion chamber is 24 inches (61 cm) in diameter, 8 feet (2.44 m) high, and is refractory lined. Vertical orientation of the combustor minimizes wall deposits and refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of coalescing or condensing fly ash. The mean residence time of a particle in the combustor is approximately 3 seconds based on superficial velocity. Combustion efficiencies of at least 99%, based upon loss-on-ignition of the fly ash and absence of CO in the flue gas, are evidence that incomplete combustion is not a problem with this test combustor. Comparison of PTC-generated fly ash with fly ash collected from a full scale plant burning the same coal, shows no major differences.

Three separate modes of operation are available with the PTC baghouse, which is illustrated in Figure 4. The first is the shaker chamber which has 3 compartments of 3 bags each for a total of 9 bags. Both shaker amplitude and frequency are adjustable. Bag cleaning is accomplished by taking 3 bags at a time off-line for shaking. The air-to-cloth ratio for the shaker mode is approximately 3 ft/min (0.9 m/min).

The other 2 modes of operation that are available both use cage-mounted bags. One of these is the pulse jet chamber which has 3 bags for an air-to-cloth ratio of 9 ft/min (2.7 m/min). In spite of the high air-to-cloth ratio, available data indicates that it is possible to operate this chamber at high efficiencies and reasonable pressure drops. The other chamber has 6 cage-mounted bags with an air-to-cloth ratio of 4.5 ft/min (1.4 m/min). This chamber uses low pressure expansion (reverse air) for cleaning. Cleaning is done on-line with 2 bags at a time being cleaned.

The PTC baghouse is designed to operate at temperatures up to 800°F (427°C). However, for this work the operating temperature was limited to 300°F (150°C). Each compartment of the baghouse is equipped with heaters so that the baghouse may be preheated to prevent condensation during startup. A more detailed description of the PTC system can be found in a previous publication (10).

Experimental Method

After startup and stabilization of any of these combustion systems, tests begin with pneumatic injection of the sorbent into the flue gas stream at a specified location with an adjustable screw feeder. Data collected during each test include system temperatures, static and differential pressures, flow rates, sorbent feed rate, and flue gas constituent concentrations (SO_2, O_2, NO_x, and CO_2). Samples collected during and after each test include sorbent feed, fly ash, baghouse hopper material, and coal (during pc-firing). Analyses of samples include surface area, particle size distribution, scanning electron microscopy, x-ray diffraction (XRD), x-ray fluorescence (XRF), and routine coal analysis.

Bench-Scale Batch Pressure Hydrator

The pressure hydrator currently in use is a bench-scale batch system capable of producing 5 lbs (2270 g) of pressure hydrated lime per run. A schematic of the pressure hydrator is presented in Figure 5. The high pressure air line pressurizes the water storage tank to 150 psig (10.3×10^5 N/m^2). The storage tank is connected to the reactor chamber by a 0.5 inch diameter (1.3 cm) stainless steel pipe. A ball valve between the reactor and the storage tank controls the rate of flow of the water into the reaction chamber. The reactor consists of an 8 inch (20.3 cm) schedule 80 carbon steel pipe that is 12 inches (30.5 cm) long with carbon steel flanges capping both ends. A paddle-wheel stirrer was installed in the reactor to mix the lime and water thoroughly. The paddle wheel rotates at 2 revolutions per minute. Ejection of the hydrated product is accomplished through a 1 inch (2.5 cm) stainless steel pipe and ball valve. An orifice plate, downstream of the ball valve, measures the gaseous flow rate of the reactor effluent. A nylon bag capable of collecting submicron size particles is clamped onto the pipe downstream of the orifice plate.

For the batch operation of the pressure hydrator, a known amount of lime (-140 mesh, 110 μm) is introduced into the reactor. The internal wall of the reactor is heated to 330°F (170°C). When the reactor is at the proper temperature, water is carefully added under pressure to the lime in the reactor. The water not reacted with the lime is vaporized, increasing the reactor pressure to approximately 100 psig (6.9×10^5 N/m^2). Due to the exothermic hydration reaction, the reactor temperature rises to about 410°F (210°C). The pressure and temperature of the reactor are monitored on a strip chart recorder.

About 20 minutes after starting water injection, the reactor temperature levels off and begins to drop. At this point, it is assumed that all of the lime has reacted to the hydrated form. The hydrated lime is then ejected from the reactor through a ball valve. The rapid expansion of the water vapor trapped in the pores of the hydrated lime during ejection is responsible for the reduction in product particle size. The gaseous flow rate is maintained at about 10 scfm (0.3 m^3/min). At this point the submicron pressure hydrated lime may be collected in a nylon bag, or injected directly into a pilot-scale combustion system.

DISCUSSION OF RESULTS

Propane-Fired Combustor/High-Temperature Baghouse System

Pilot-scale evaluation of direct in-furnace injection of calcium-based sorbents began in 1978. Results of those early tests indicated that better SO_2 reduction and sorbent utilization could be achieved with a hydrated lime than with limestone or quicklime.

Hydrated lime injection tests were performed to investigate the effects of flue gas injection point temperature, baghouse temperature, and Ca/S ratio on SO_2 reduction. A commercial slaked calcitic hydrated lime was the primary sorbent used with a few tests conducted with a commercial dolomitic hydrated lime. All the hydrated lime used during the test series was air classified to -325 mesh (<44 μm).

Baghouse temperature, air-to-cloth ratio, and SO_2 levels were nominally constant at 900°F (480°C), 6.3 ft/min (1.9 m/min), and 650 ppm, respectively. Fly ash was continuously injected into the flue gas at a rate of approximately 2.0 gr/scf (4.6 g/m^3) to provide a filter cake on the ceramic bags. X-ray fluorescence data for the commercial slaked calcitic hydrated lime showed calcium oxide (CaO) content was approximately 58% by weight. Surface area prior to injection was approximately 10.0 m^2/g. X-ray fluorescence data for the dolomitic hydrated lime showed calcium oxide (CaO) and magnesium oxide (MgO) content were approximately 40% and 30%, respectively. Surface area of the dolomitic hydrated lime was about 15.0 m^2/g prior to injection. Stoichiometric ratios were based on the CaO content of the respective sorbents.

Sulfur dioxide reduction and sorbent utilization data for the commercial slaked calcitic hydrated lime are presented as a function of flue gas injection point temperature in Figures 6 and 7, respectively. Figure 6 shows that SO_2 reduction for Ca/S ratios of 0.8 to 1.33 increased from about 15% to 40% as injection temperature increased from 1650° to 2600°F (900° to 1425°C). The curve begins to level off at injection temperatures ranging from 2300° to 2800°F (1260° to 1540°C) indicating a maximum SO_2 reduction of 40% to 50% for the range of Ca/S ratios stated above. The SO_2 reduction profile for the Ca/S range of 1.5 to 2.2 was similar, although the curve was slightly higher. Improved SO_2 reduction with increasing injection temperature may be attributed to an increase in the particle residence time in the temperature regime where SO_2-CaO reaction kinetics are significant (1600°-2200°F, 870°-1200°C). These results were achieved at temperatures higher than those reported by other investigators and are probably attributable to the short particle residence times at high temperatures (2200°-2800°F, 1200°-1540°C) in the propane-fired combustor system.

Hydrated lime utilization increased with increasing flue gas injection point temperature for two Ca/S ranges, as shown in Figure 7. Utilization values increased from about 13% to 40% as injection temperature increased from 1650° to 2820°F (900° to 1550°C) for Ca/S ratios ranging from 0.8 to 1.2. Higher Ca/S ratios, 1.5 to 2.2, showed the same trend but, the curve was slightly lower at temperatures above 2000°F (1095°C).

The effect of baghouse temperature on SO_2 reduction and hydrated lime utilization is presented in Figure 8. Injection point temperature and air-to-cloth ratio were nominally constant at 2800°F (1540°C) and 5.8 ft/min (1.7 m/min), respectively. Both SO_2 reduction and hydrated lime utilization increased slightly, ∿5%, as the baghouse temperature increased from 700° to 900°F (370° to 480°C). Figure 9 illustrates total hydrated lime utilization, and hydrated lime utilization within the baghouse, as a function of baghouse temperature. Injection point temperature and air-to-cloth ratio were nominally constant at 2850°F (1570°C) and 5.8 ft/min (1.7 m/min), respectively. Total hydrated lime utilization increased from 30% to 35% as the baghouse temperature increased from 700° to 900°F (370° to 480°C). For the same temperature range, utilization within the baghouse increased from 5% to 10%.

Sulfur dioxide reduction and sorbent utilization data for the commercial dolomitic hydrated lime are presented as a function of injection point temperature in Figure 10. Ca/S ratios ranged from 1.8 to 2.9. Both SO_2 reduction and sorbent utilization show a 50% increase as injection temperature increased from 1800° to 2075°F (980° to 1135°C). Sulfur dioxide reduction also increased significantly as injection temperature increased from 2075° to 2460°F (1135° to 1350°C), but this change is more a result of the variable Ca/S ratio than injection temperature. Sorbent utilization values show essentially no change for injection temperatures above 2075°F (1135°C). In this case the variability of the Ca/S ratios is masking small increases in utilization which would be expected. Direct comparison of results indicate the commercial slaked calcitic hydrate may be as good or a better candidate for SO_2 control even though the commercial dolomitic hydrate was found to have a higher initial surface area.

Ash Fouling Combustor/High-Temperature Baghouse System

As a result of the initial injection tests on the propane-fired system, subsequent experiments for the simultaneous SO_x/NO_x control program have focused on the use of hydrated lime. Specifically the use of a pressure hydrator is being evaluated.

The hydrated product from the bench-scale batch pressure hydrator developed at UNDERC was found to be dry, and x-ray diffraction and scanning electron microscopy showed the product to be 100% hydrated with an average particle size of less than 1.0 µm. Figures 11 and 12 illustrate that complete hydration of CaO to $Ca(OH)_2$ occurs in the pressure hydrator.

Figure 13 presents SO_2 reduction as a function of flue gas injection point temperature for a series of 6 tests performed on the ash fouling combustor/high-temperature baghouse system firing pulverized coal. Baghouse temperature, air-to-cloth ratio, SO_2 levels, and Ca/S ratio were nominally constant at 940°F (505°C), 3.0 ft/min (0.9 m/min), 700 ppm, and 1.0, respectively. The sorbent used was a calcitic pressure-hydrated lime produced in the bench-scale pressure hydrator. Two sets of data are presented in Figure 13. The upper curve depicts total SO_2 reduction and the lower curve SO_2 reduction within the high-temperature baghouse.

Sulfur dioxide reduction in the baghouse never exceeded 7% for the six tests performed. Low SO_2 reduction in the baghouse is consistent with previous results. Operation of a baghouse at temperatures ranging from 800° to 1000°F (425° to 540°C) may not increase utilization of calcium-based sorbents enough to warrant use of a high-temperature baghouse only for SO_2 control. But in combination with a NO_x control technique, the 5% to 10% increase in sorbent utilization may be significant.

Maximum total SO_2 reduction was approximately 55% at an injection point temperature of about 1900°F (1040°C). Lower SO_2 reduction at injection temperatures below 1900°F (1040°C) was probably a result of insufficient residence time in the flue gas temperature region where SO_2-CaO reaction kinetics are most favorable. As injection temperature increased from 1900°F (1040°C), SO_2 reduction again decreased. This decrease may have been caused by sintering of the sorbent particles (reduced surface area development) or some interaction with the fly ash. Although fly ash interference is possible, injection tests performed at UNDERC have not shown fly ash interference to be a problem. Figure 14 presents SO_2 reduction as a function of injection temperature for a series of natural gas-fired injection tests. Although the curve is similar to that in Figure 13, actual SO_2 reduction is slightly lower for tests performed during natural gas-firing.

A single injection test was conducted at conditions similar to those presented in Figure 13 except the Ca/S ratio was increased from 1.0 to 2.0. The flue gas injection point temperature was ∿1900°F (1040°C). Sulfur dioxide reduction and calcium utilization were about 80% and 40%, respectively. Figure 15 illustrates SO_2 concentration as a function of time for the two-hour injection test. The peaks observed at 65, 110, and 145 minutes were caused by inconsistencies in the sorbent feed rate. From 60 to 180 minutes, average SO_2 concentration decreased approximately 100 ppm. This decrease is believed to be partially a function of SO_2 reduction within the baghouse and sorbent fallout in the refractory-lined flue ducts of the AF/HTB system.

Two injection tests were performed at Ca/S ratios of 1.0 but at SO_2 levels of 1300 and 3000 ppm. Results from these tests, presented in Table 1, showed SO_2 reduction remained in the 45 to 50% range for the higher SO_2 levels. Injection tests have not yet been performed at Ca/S ratios exceeding 1.0 for SO_2 levels greater than 1000 ppm.

A single injection test was also performed using a commercial dolomitic hydrated lime. The specific sample used for this test was collected from a commercial hydration facility prior to ball milling. Test conditions and SO_2 reduction data are presented in Table 1 (Test No. 0484.9). The resulting SO_2 reduction for this test was about 40%, as compared to the 55% value obtained with the calcitic pressure hydrated lime produced in the UNDERC bench-scale pressure hydrator. Without further testing, it is not clear whether this difference is due to the composition of the dolomitic hydrate (presence of MgO), or to the difference in pressure hydration conditions.

Test results from the AF/HTB system were different from those obtained from the propane-fired system in that maximum SO_2 reduction and hydrated lime utilization were observed when injecting the hydrated lime into a temperature regime of about 1900°F (1040°C) rather than 2800°F (1540°C). This indicates the overall time/temperature profile of the AF/HTB system was more favorable at lower flue gas temperature than those reported for the propane-fired system. Hydrated lime utilization values of 40% to 55% were observed in both systems for Ca/S ratios ranging from 0.8 to 2.0.

Particulate Test Combustor System

A review of the data generated on the AF/HTB system resulted in a decision to perform subsequent pilot-scale injection tests on the particulate test combustor (PTC) rather than the AF/HTB system. Reasons for this decision included: 1) the availability of the system (fewer projects sharing time on same pilot-scale system), 2) the PTC is better suited for evaluation of additive-enhanced pressure hydrated lime sorbents, and 3) the high-temperature baghouse showed no significant advantage with respect to SO_2 control alone (the PTC baghouse typically operates at more conventional temperatures, 200° to 500°F (95° to 260°C)).

The purpose of the initial series of in-furnace injection tests on the PTC system was to generate morphological (surface area and particle size distribution) and SO_2 reduction data for calcitic and dolomitic pressure-hydrated lime. Calcitic pressure-hydrated lime used in this test series was produced in the bench-scale pressure hydrator. The dolomitic hydrate was obtained from a commercial source. Injection tests performed to generate morphological data were conducted firing natural gas to produce an SO_2-free flue gas stream. A Beulah lignite was used during pc-fired injection tests.

Surface area data were not all available for inclusion in this paper. Evaluation of particle size distribution data (as determined from multicyclone sampling) from dehydrated sorbent samples collected during injection tests using calcitic and dolomitic pressure-hydrated lime indicates 90% of the particle mass to be larger than 2 μm. It is believed this observation is a result of the agglomeration of submicron particles. Multicyclone samples have been submitted for analysis using SEM techniques.

Direct comparison of SO_2 reduction data from the PTC and AF/HTB systems was made at similar combustor operating conditions. The most significant differences in the two systems were baghouse operating temperature and flue gas duct configuration downstream of the combustor. Typically the PTC baghouse operates at ∿300°F (∿150°C) compared to 900° to 1000°F (480° to 540°C) for the AF/HTB system. Flue gas ducting downstream of the PTC combustor was designed to minimize particulate fallout whereas the AF flue gas ducting has 5 90°-bends resulting in particulate fallout.

A comparison of SO_2 reduction data from the two systems as a function of injection point temperature during natural gas-firing is illustrated in Figure 16. Although the data from the two systems result in similar curves, SO_2 reduction in the PTC system appears to average about 10% higher for the range of injection temperatures evaluated, 1300° to 2700°F (700° to 1480°C). Table 2 presents SO_2 reduction data for the PTC and AF/HTB systems generated during pc-fired injection tests. Again, direct comparison of SO_2 reduction data generated at similar test conditions shows slightly better results were achieved in the PTC system. These data might therefore indicate the time/ temperature profile of the PTC system is better than the AF/HT system with respect to SO_2 reduction. Reduced sorbent fallout may also have contributed to better SO_2 reduction observed in the PTC system.

CONCLUSIONS

Direct furnace injection of calcitic pressure-hydrated lime is capable of 80% SO_2 reduction at a Ca/S ratio of 2.0 in the UNDERC pilot-scale combustion systems.

Calcitic pressure hydrated lime produced in a bench-scale pressure hydrator was found to be a better sorbent for SO_2 reduction than the commercial dolomitic pressure-hydrated lime.

Operation of a baghouse at temperatures up to 1000°F (540°C) does not increase utilization of calcium-based sorbents enough to warrant use of a high-temperature baghouse only for SO_2 control. But in combination with a NO_x control technique, the 5% to 10% increase in sorbent utilization may be considered significant.

As expected, residence time and the temperature regime of the sorbent injection location appear to be the critical parameters controlling SO_2 reduction and sorbent utilization.

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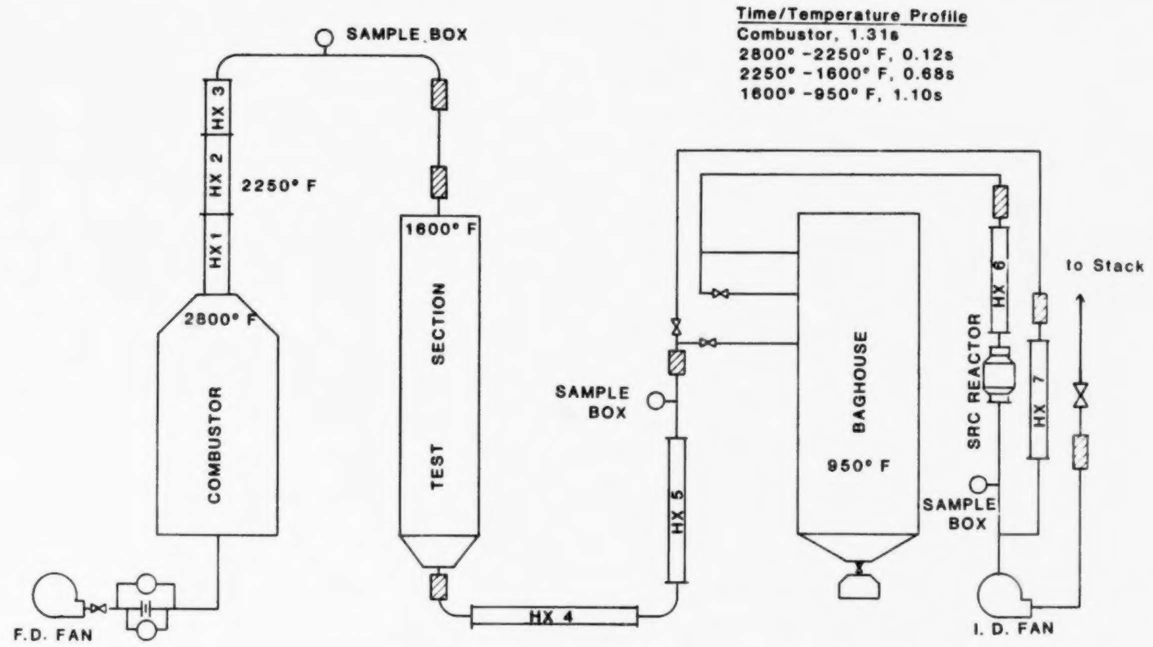
Time/Temperature Profile
Combustor, 1.31s
2800° -2250° F, 0.12s
2250° -1600° F, 0.68s
1600° -950° F, 1.10s
SAMPLE BOX
HX 3
HX 2
HX 1
2250° F
2800° F
COMBUSTOR
F.D. FAN
1600° F
TEST SECTION
HX 4
SAMPLE BOX
HX 5
BAGHOUSE
950° F
HX 6
SRC REACTOR
HX 7
SAMPLE BOX
I. D. FAN
to Stack

Figure 1. Propane-fired combustor/high-temperature baghouse system.

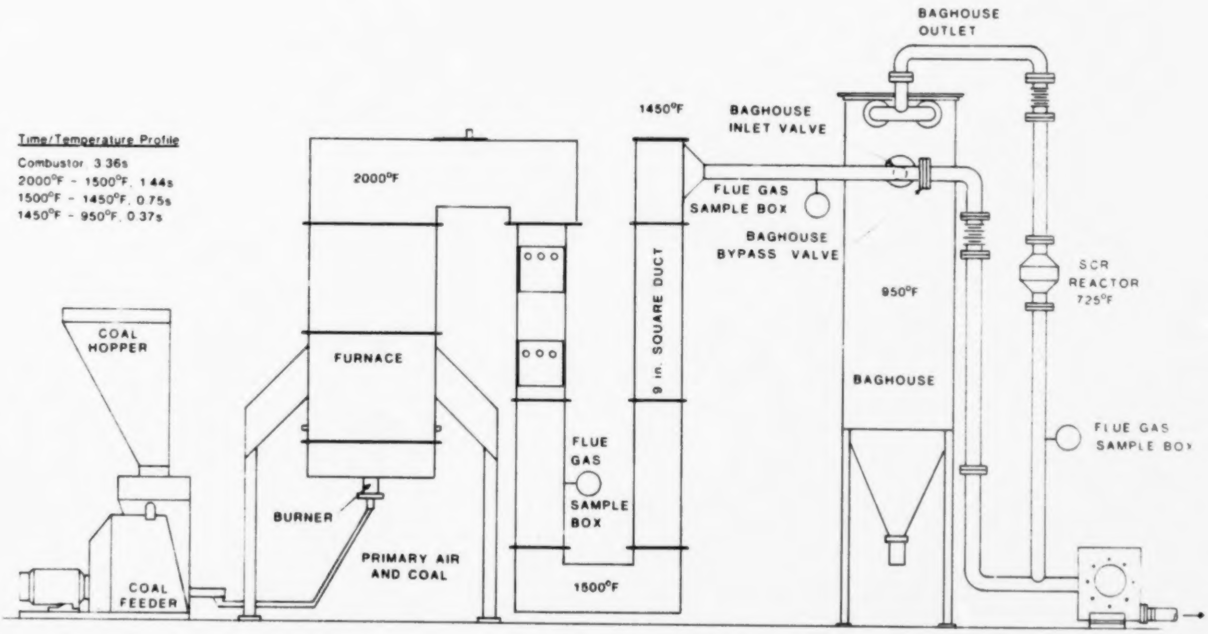
Time/Temperature Profile
Combustor 3.36s
2000°F - 1500°F, 1.44s
1500°F - 1450°F, 0.75s
1450°F - 950°F, 0.37s
COAL HOPPER
COAL FEEDER
2000°F
FURNACE
BURNER
PRIMARY AIR AND COAL
FLUE GAS SAMPLE BOX
1500°F
9 in. SQUARE DUCT
1450°F
BAGHOUSE INLET VALVE
FLUE GAS SAMPLE BOX
BAGHOUSE BYPASS VALVE
BAGHOUSE OUTLET
950°F
BAGHOUSE
SCR REACTOR 725°F
FLUE GAS SAMPLE BOX

Figure 2. Ash fouling combustor/high-temperature baghouse system.

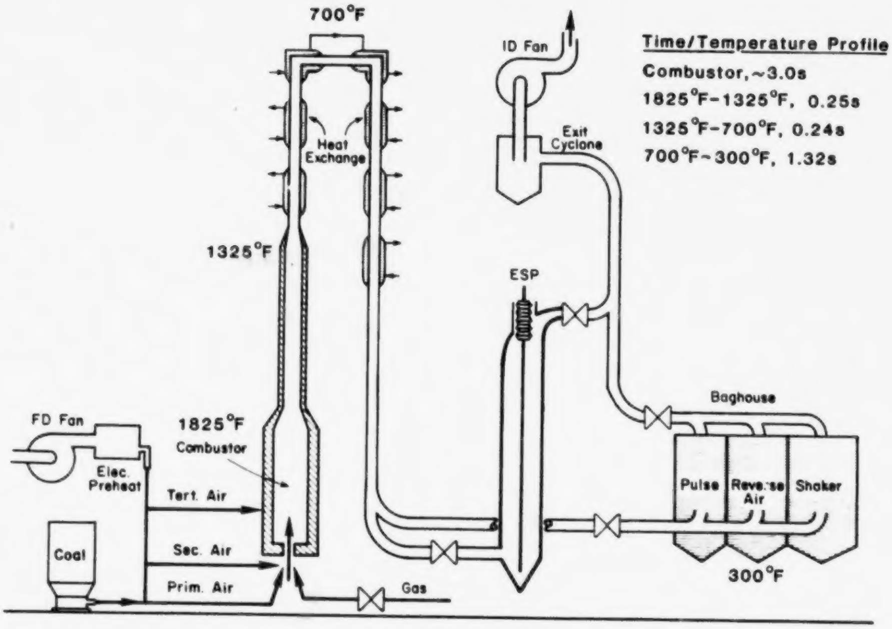
700°F
ID Fan
Time/Temperature Profile
Combustor,~3.0s
1825°F-1325°F, 0.25s
1325°F-700°F, 0.24s
700°F-300°F, 1.32s
Heat Exchange
Exit Cyclone
1325°F
ESP
Baghouse
FD Fan
1825°F
Combustor
Elec. Preheat
Tert. Air
Pulse
Reverse Air
Shaker
Coal
Sec. Air
Prim. Air
Gas
300°F

Figure 3. The particulate test combustor, a 500,000 Btu/hr pc-fired furnace.

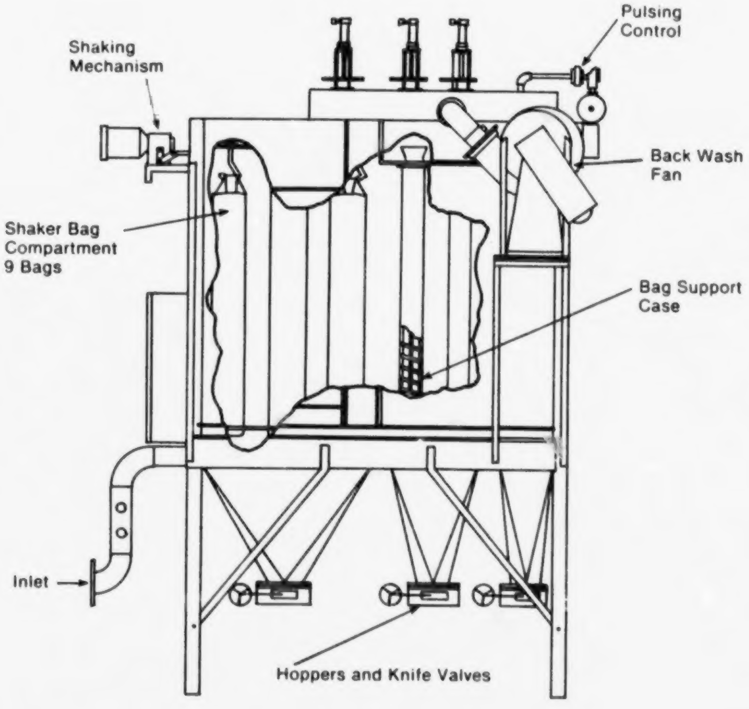
Pulsing Control
Shaking Mechanism
Back Wash Fan
Shaker Bag Compartment 9 Bags
Bag Support Case
Inlet
Hoppers and Knife Valves

Figure 4. Three-mode experimental baghouse, a 200 ACFM pilot facility operating in shaker, low pressure expansion (cage-mounted reverse air) or pulse mode.

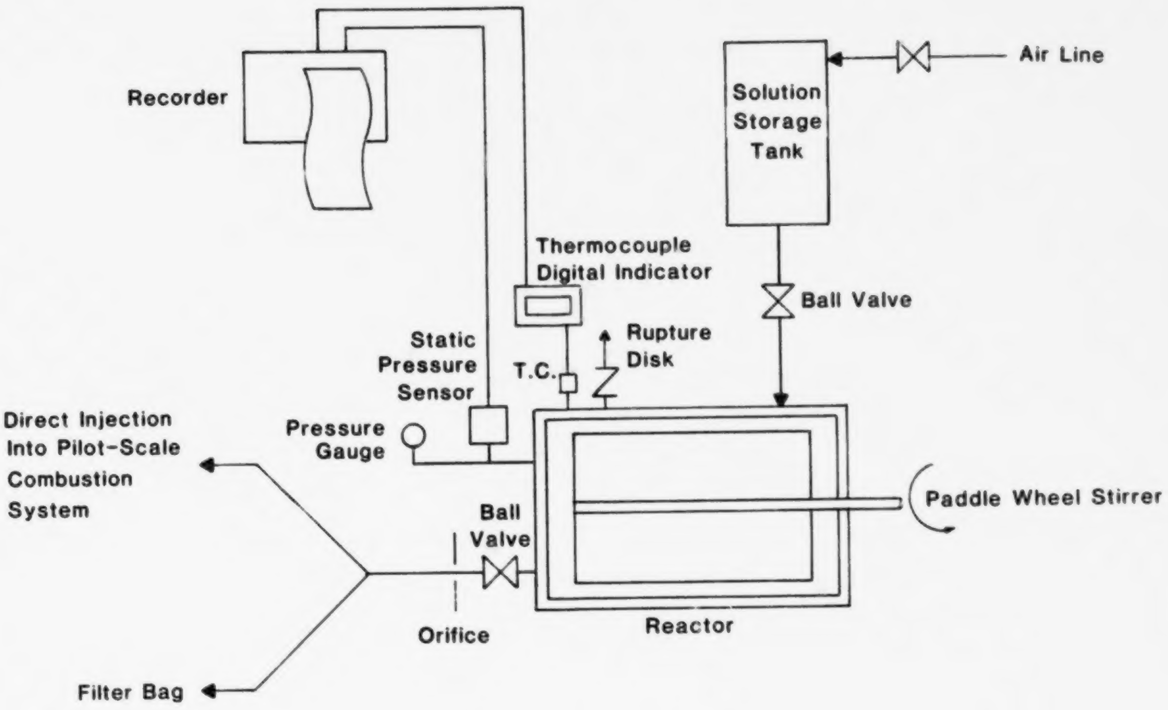
Recorder
Solution Storage Tank
Air Line
Thermocouple Digital Indicator
Ball Valve
Static Pressure Sensor
Rupture Disk
T.C.
Direct Injection Into Pilot-Scale Combustion System
Pressure Gauge
Paddle Wheel Stirrer
Ball Valve
Orifice
Reactor
Filter Bag

Figure 5. Basic components of the bench-scale batch pressure hydrator.

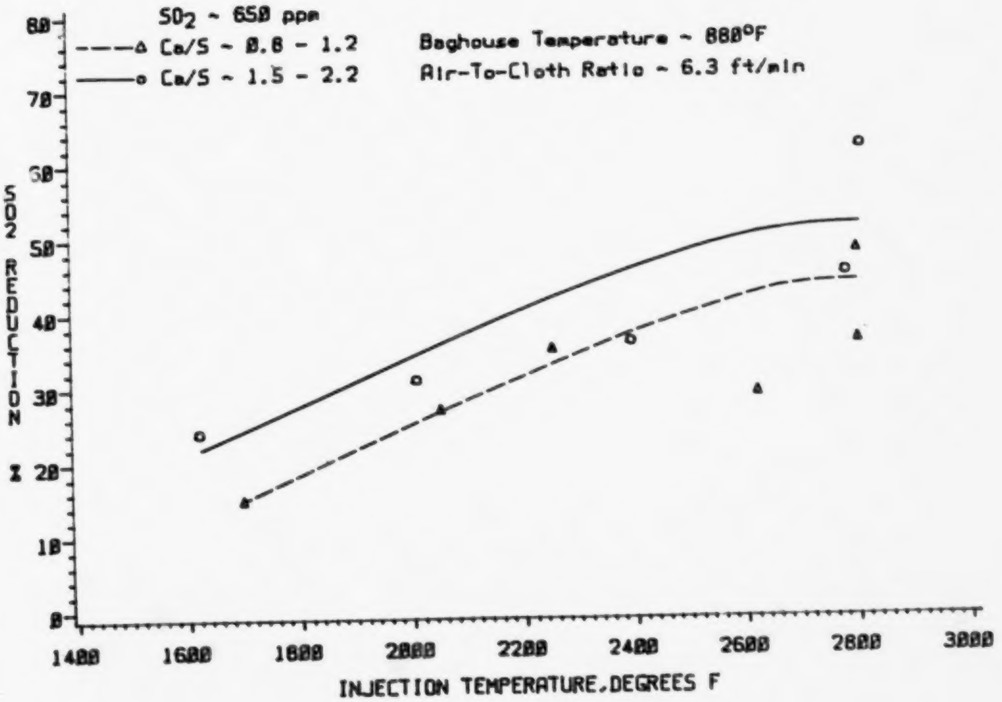

Figure 6. Sulfur dioxide retention versus flue gas injection point temperature.

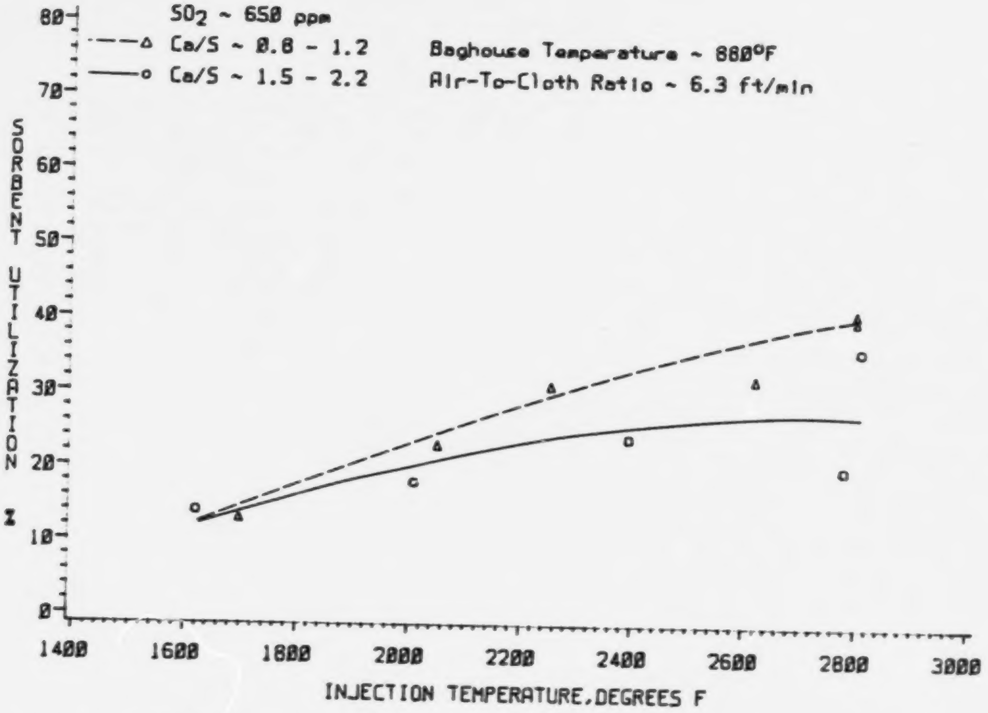

Figure 7. Utilization of slaked calcitic hydrated lime versus flue gas injection point temperature.

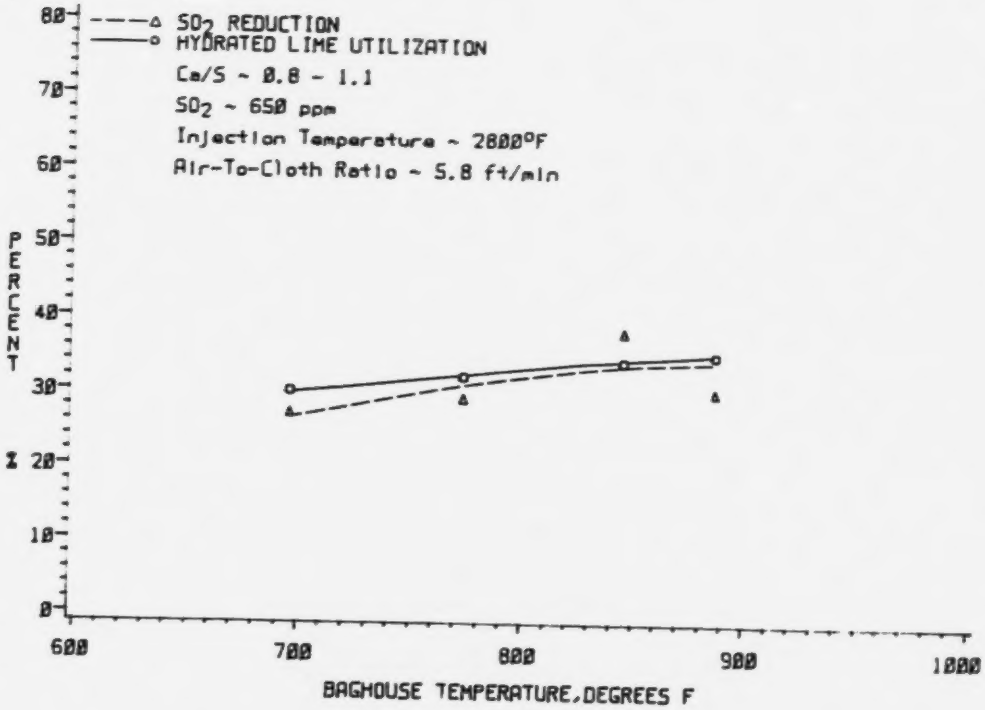

Figure 8. Sulfur dioxide reduction and utilization of slaked calcitic hydrated lime versus baghouse temperature.

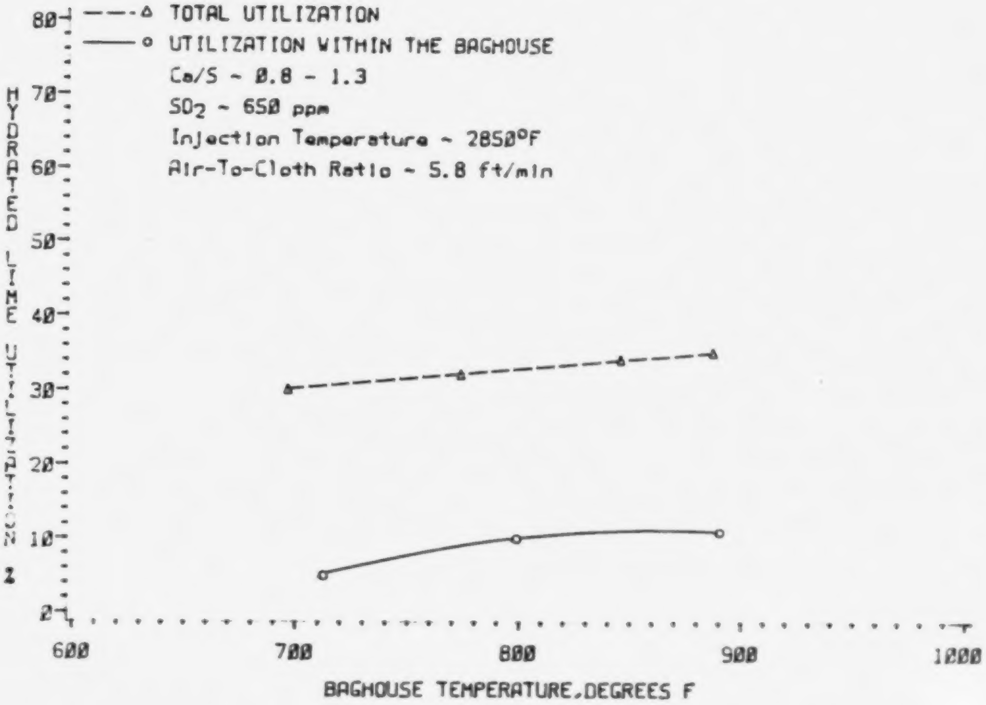

Figure 9. Utilization of slaked calcitic hydrated lime versus baghouse temperature.

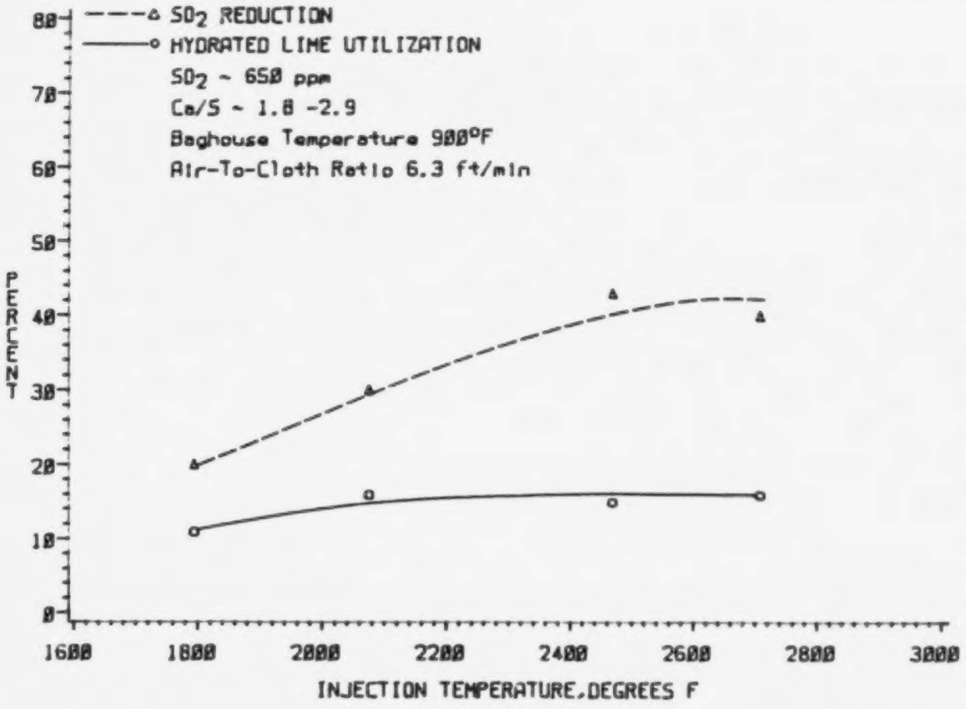

Figure 10. Sulfur dioxide reduction and dolomitic hydrated lime utilization versus flue gas injection point temperature.

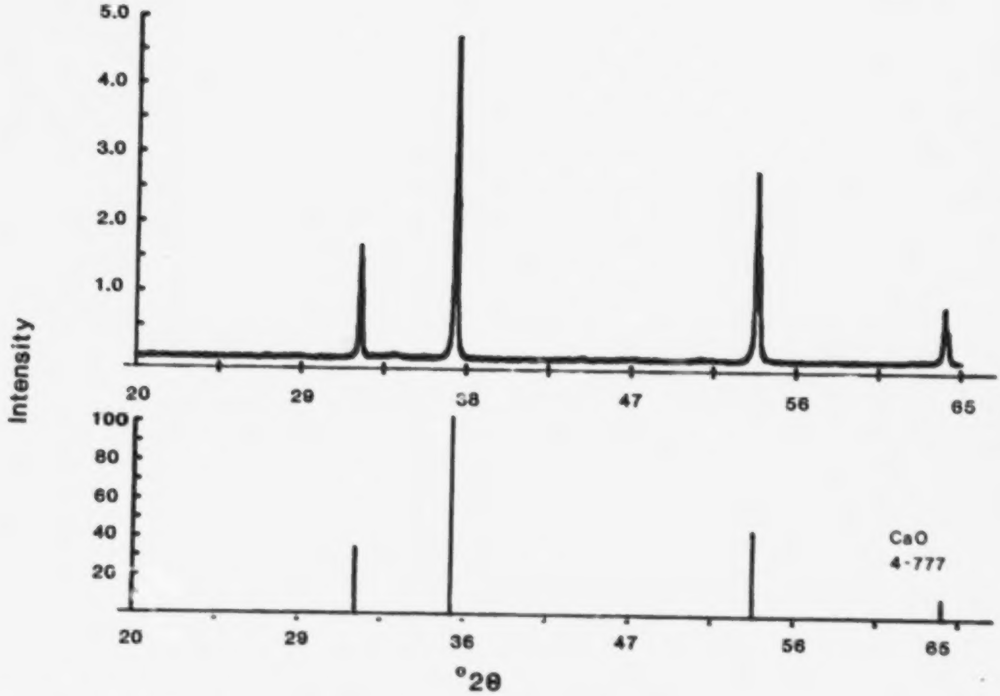

Figure 11. X-ray diffraction scan of quicklime feed to pressure hydrator.

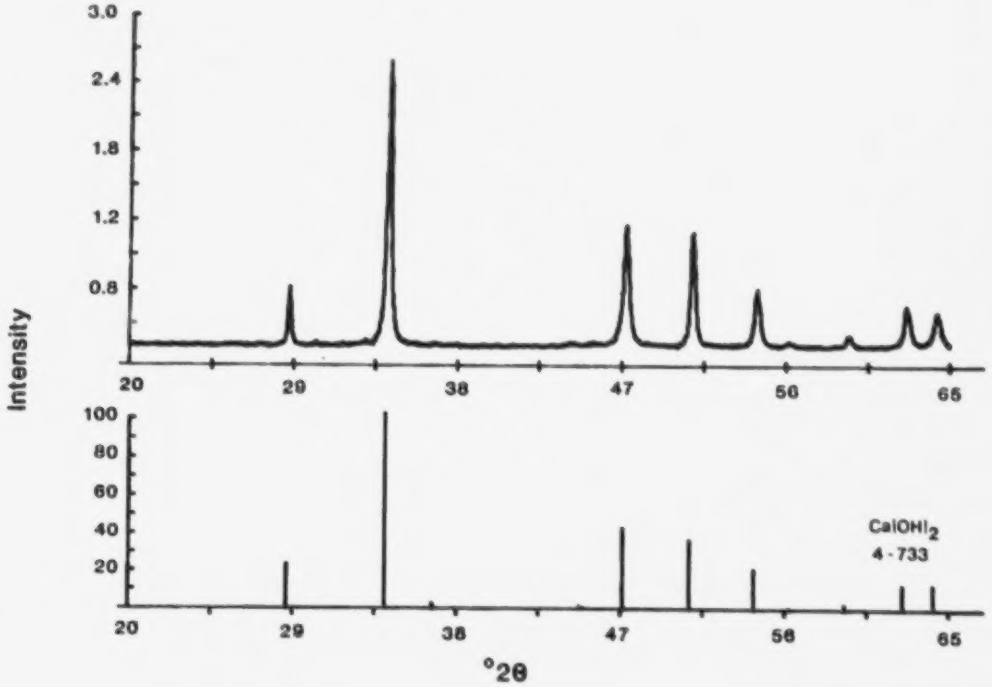

Figure 12. X-ray diffraction scan of hydrated product from pressure hydrator.

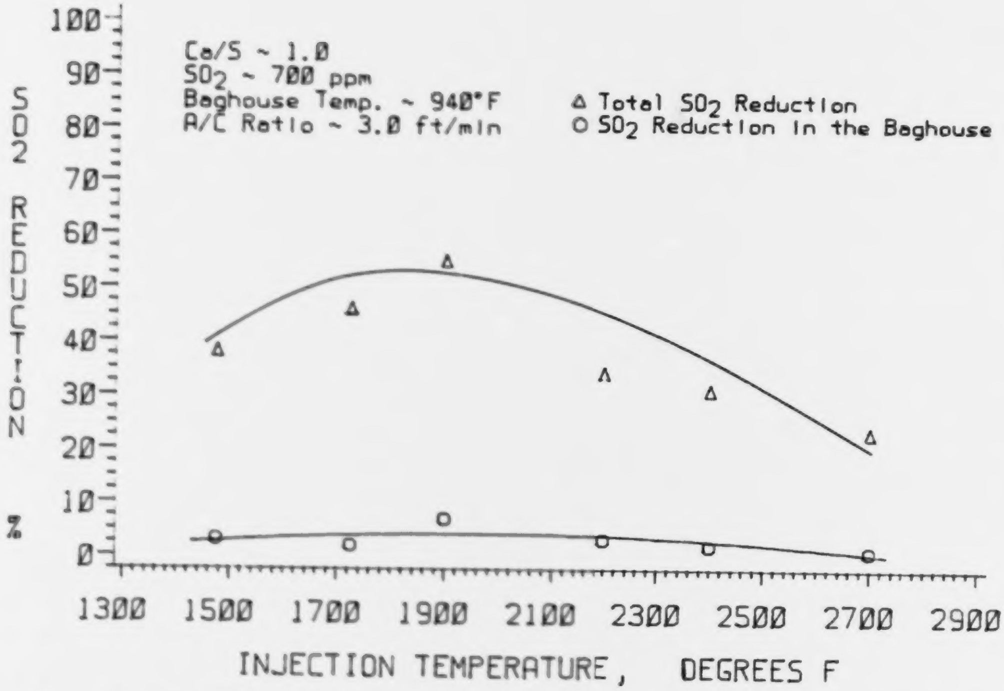

Figure 13. Sulfur dioxide reduction versus injection temperature for the ash fouling combustor/high-temperature baghouse system.

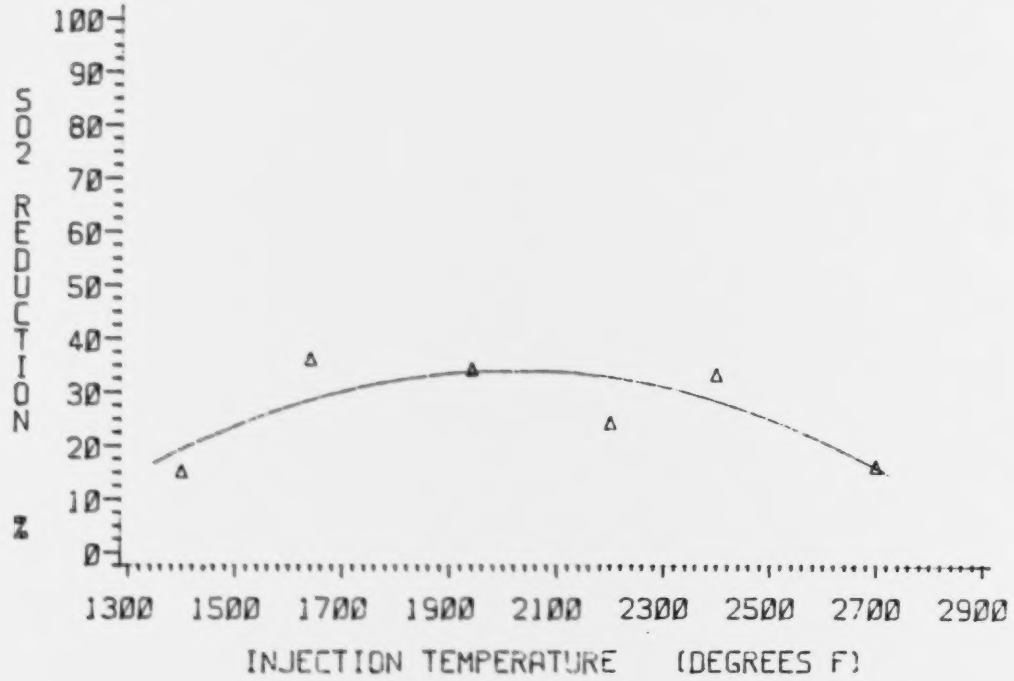

Figure 14. Sulfur dioxide reduction versus injection temperature for natural gas-fired injection tests.

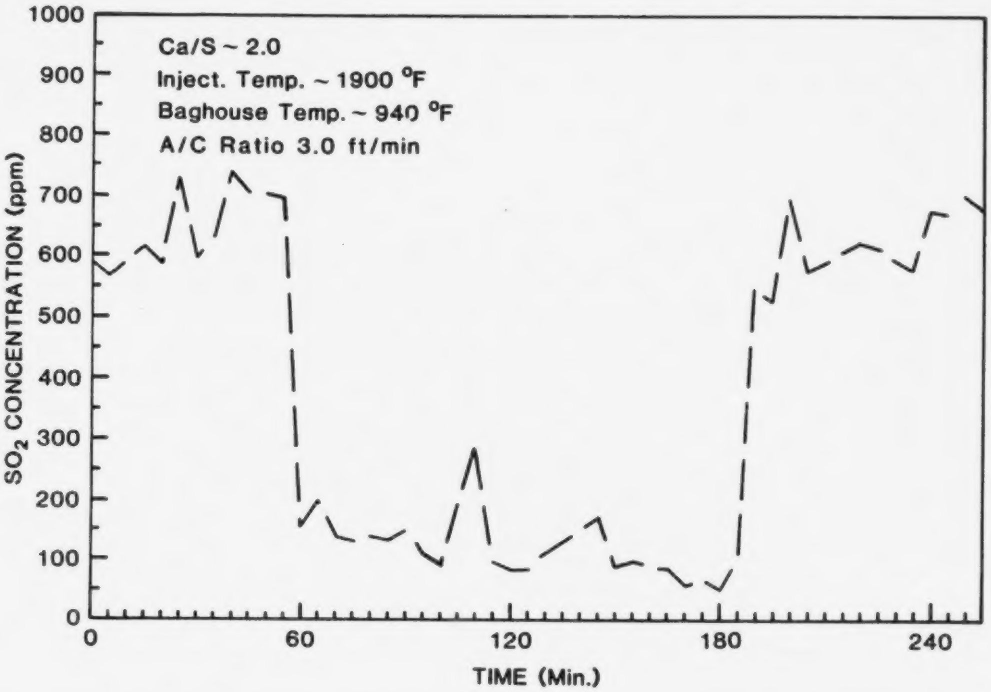

Figure 15. Sulfur dioxide concentration versus time for a calcitic pressure hydrated lime injection test on the pc-fired combustor/high-temperature baghouse system.

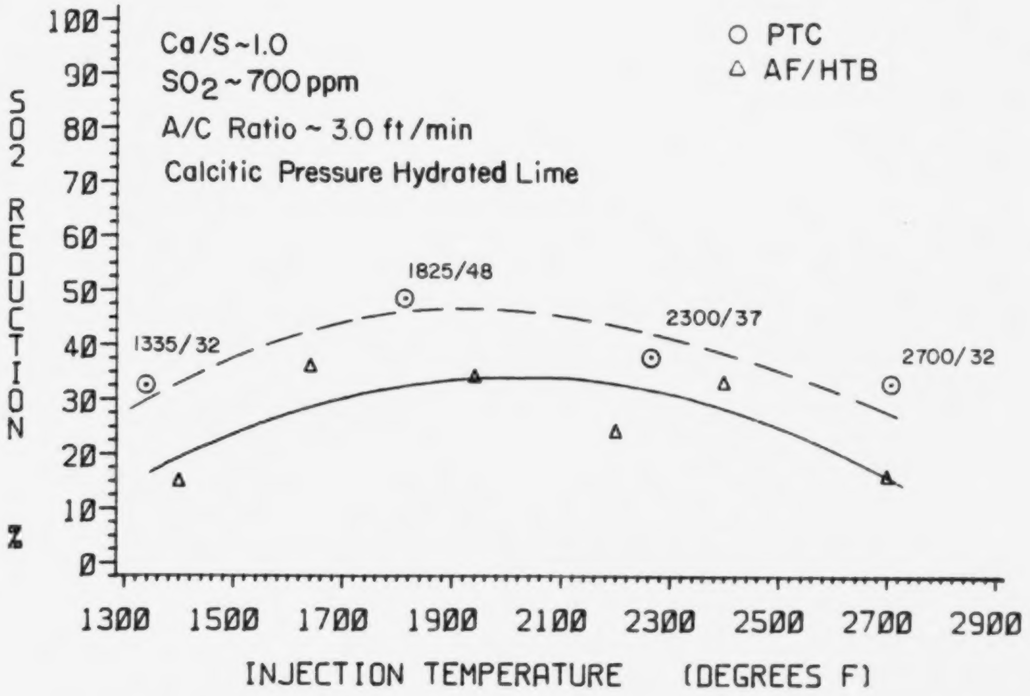

Figure 16. Sulfur dioxide reduction versus injection temperature for natural gas-fired injection tests.

TABLE 1

PRESSURE HYDRATED LIME SO_2 REDUCTION DATA[a]

Test No.[b]	Total SO_2 Reduction, %	SO_2 Conc. ppm	Ca/S	Sorbent Utilization, %
0584.1	55	725	1.0	55
0584.5	45	1320	1.0	45
0584.7	48	3000	1.0	48
0484.9	40	740	1.0	40

[a] Injection temperature, baghouse temperature, and air-to-cloth ratio were nominally 1900°F, 940°F, and 3.0 ft/min, respectively.

[b] The sorbent used in tests 0584.1, 0584.5, and 0584.7 was a calcitic pressure hydrated lime (75% CaO) produced in the bench-scale pressure hydrator. The sorbent used in test 0484.9 was a commercial dolomitic pressure hydrate (40% CaO and 30% MgO).

TABLE 2

SO_2 REDUCTION DATA[a]

Test No.[b]	Pilot Scale System	SO_2 Conc. ppm	Total SO_2 Reduction, %	Ca/S	Sorbent Utilization, %
0584.1	AF/HTB	725	55	1.0	55
1184.1	PTC	920	45	0.7	64
0484.8	AF/HTB	700	80	2.0	40
1284.1	PTC	1000	74	1.7	44
0484.9	AF/HTB	740	40	1.0	40
1084.1	PTC	870	40	0.8	50

[a] Injection temperature and air-to-cloth ratio were nominally 1900°F and 3.0 ft/min, respectively.

[b] The sorbent used in tests 0584.1, 1184.1, 0484.8, and 1284.1 was a calcitic pressure hydrated lime (75% CaO) produced in the bench-scale pressure hydrator. The sorbent used in tests 0484.9 and 1084.1 was a commercial dolomitic pressure hydrate (40% CaO and 30% MgO).

BENCH SCALE PROCESS EVALUATION OF IN-FURNACE NO_x AND SO_x REDUCTION BY REBURNING AND SORBENT INJECTION

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M. P. Heap, and W. R. Seeker
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Irvine, CA 92718-2707

ABSTRACT

Reburning involves the injection of a secondary fuel above the main firing zone of a combustion to produce a reducing zone which acts to reduce NO_x to molecular nitrogen. Overfire air is added above the reburn reducing zone to complete the combustion. The reburning process has been combined with the injection of calcium-based sorbents (e.g., limestone) to investigate the potential for combined NO_x and SO_x reduction. Bench scale evaluations of the process carried out in a plug flow furnace at 23 kW_t have indicated that NO_x reductions of up to 70 percent and sulfur captures of up to 50 percent (at Ca/S = 2) can be achieved depending on a number of process variables. The dominant variables include the initial NO_x level that is to be reduced, the reburning fuel type (pulverized coal or natural gas), and the residence time and temperature in the reducing zone. For sulfur control, the dominant parameters are the amount of sorbent added, the sorbent type, and the injection temperature.

INTRODUCTION

This paper addresses the reburning technology which removes NO from combustion products using fuel as the reducing agent. It has been found to involve similar kinetic processes to those involved in combustion modification by staged combustion. This technology is variously referred to as:

- In-furnace NO_x reduction
- Reburning
- Staged fuel injection
- Mitsubishi Advanced Combustion Technology (MACT)

Reburning can be considered as the process which allows in-furnace NO_x reduction to take place.

The concept of NO reduction by flames has been known for over a decade. A flue gas NO_x incinerator was developed by the John Zinc Company (1), and Wendt, Sternling, and Matovich (2) found that NO could be reduced in laboratory flat flames by injecting methane into the combustion products. Recently, Japanese investigators have reported the application of reburning to large test furnaces (3). The MACT (Mitsubishi Advanced Combustion Technology) in-furnace NO_x removal process applies the concept of reburning to a boiler. Part of the fuel bypasses the main heat release zone and is injected above the main burners to provide the fuel for reburning. It is claimed that the NO_x produced by the main firing system can be reduced "to half at any level of concentration" (3). Hitachi Shipbuilding and Engineering has a U.S. patent on multistage fuel injection for NO_x control (4). EER under contract to the U.S. Environmental Protection Agency has been investigating the reburning process as it might be applied to U.S.-designed pulverized coal utility boilers for the last few years. The initial activity has involved bench scale testing of the impact of process variables on the NO_x removal efficiency. The studies have been performed in tower furnaces that allow control of process parameters over the range of interest in utility boiler furnaces. The reburning process can be divided into three zones:

- Primary Zone: This main heat release zone accounts for approximately 80 percent of the total heat input to the system. The zone is operated under overall fuel-lean conditions, although the burners might be low-NO_x distributed mixing burners. The level of NO_x exiting from this zone is the level to be reduced in the reburning process.

- Reburning Zone: The reburning fuel (normally about 20 percent of the total fuel requirements) is injected downstream of the primary zone to create a fuel-rich reduction zone. The reactive nitrogen entering this zone comes from two sources: The primary NO level and the fuel nitrogen in the reburning fuel. These fuel nitrogen species apparently react with the hydrocarbon fragments from the reburning fuel to produce intermediate species such as NH_3 and HCN while some is converted to N_2 and some is retained as NO. The products of this reduction zone are the reactive nitrogen species such as: NO, char nitrogen, NH_3, and HCN, which will be referred to as total fixed nitrogen (TFN). In order to optimize the NO reduction by reburning, it is necessary to minimize the total reactive nitrogen exiting the reburning zone.

- Burnout Zone: In the burnout zone, air is added to produce overall lean conditions which oxidizes all the remaining fuel and converts the total reactive nitrogen either to NO or N_2.

The reburning process can be combined with the injection of calcium containing sorbents such as limestone, to achieve simultaneous NO_x and SO_x control. Calcium oxides, which are formed when calcium carbonate decomposes, can react with gaseous SO_2 to form calcium sulfate ($CaSO_4$). The calcium sulfate particles can then be removed with the ash particles using the normal particulate removal systems. The sorbent injection process is very compatible with reburning since the addition of the reburning fuel and overfire air provides excellent media for transporting the sorbent in the upper zone of the furnace. There are similar requirements to disperse the sorbent and the reburning fuel and burnout air.

The processes that take place in each of these zones have been recently evaluated in terms of the reduction of total reactive nitrogen and gaseous sulfur (5). This paper will summarize the major findings of that study. Based on these results, a process model is currently under development which will allow an assessment to be made of the effectiveness of applying reburning/sorbent technology for different fuel types and applications.

EXPERIMENTAL

The process studies were carried out in the refractory lined Control Temperature Tower (CTT) which is shown schematically in Figure 1. The CTT has a total firing rate of between 18 and 24 kW (60,000-80,000 Btu/hr) in the main combustion chamber. The main combustion chamber is 20.3 cm in diameter and includes a long quarl entry to promote flame stabilization and to provide for one-dimensional plug flow. The time/temperature profile along the furnace could be manipulated by using back-fired heating sections. The back-fired sections consist of natural gas burners fired into refractory channels in the direction opposite to the main chamber. The high-temperature gases pass through the channels surrounding the main chamber (see the radial cross-sectional view in Figure 1) and minimize the temperature decay along the furnace. A more rapid temperature decline can be achieved by leaving the back-fired channels off or by inserting cooling coils around the main chamber. The tower is equipped with numerous ports located along the axis of the reactor that allow the installation of zone separation chokes, fuel and air injectors, cooling coils, and sampling probes.

The CTT was configured into three zones: (1) the primary zone was formed using a premixed burner firing pulverized coal or propane doped with various levels of H_2S and NO, under lean conditions (typically 10 percent excess air); (2) the reburning zone formed by injecting the reburning fuel (either coal or doped gas) at various flow rates to control the reburning zone stoichiometry and; (3) the burnout zone in which air was injected to bring the overall stoichiometry to typically 25 percent excess air. The parameters in each of these zones were examined separately in terms of how they influenced the exhaust level of NO_x. The test series were performed by establishing the level of NO_x from the primary and then increasing the amount of reburning fuel addition and burnout air correspondingly to decrease the reburning zone stoichiometry and maintain the overall burnout zone stoichiometry. In this manner, the residence time and temperature in the reburning zone were maintained relatively constant while the reburning zone stoichiometry was varied. Sorbent injection was carried out for a variety of different sorbents injected with the reburning fuel and with the burnout air.

Both flue gas and in-combustor measurements were made of NO_x, O_2, CO/CO_2, SO_2, HCN, and NH_3 by techniques presented in Table 1. In addition, the gas temperature was measured throughout the reactor by using a suction pyrometer (Type B thermocouple). Details of sampling and analysis procedures and test conditions are available elsewhere (Greene et al., 1985).

The bench scale testing has provided fundamental insight into the chemical processes that control NO_x reduction and sulfur capture and the impact of the key process variables. The full range of parameters in each zone was investigated:

- Primary Zone
  - Stoichiometry
  - Fuel type
  - NO level
  - SO_2 level

- Reburning Zone
  - Stoichiometry
  - Mixing rate of reburning fuel
  - Reburning fuel type (propane, hydrogen, CO, and coals)
  - Nitrogen content of reburning fuel
  - Temperature
  - Residence time
  - Transport media for reburning fuel (air or inert)

- Burnout Zone
  - Temperature
  - Excess air
  - Air mixing rate

For the SO_2 capture studies, the additional variables included:

- Sorbent type
- Injection location
- SO_x concentration
- Temperature profile
- Additives

RESULTS--NO_x

Although most of the parameters investigated had some effect on the reduction level achieved by the reburning process, the dominant parameters were found to be those associated with the reburning zone condition and the primary zone NO level. Figure 2 shows the effect of three parameters: reburning fuel type (propane or Utah bituminous coal), primary zone NO_x level $[(NO_x)_p]$, and reburning zone stoichiometry (SR_2). These data were taken at the baseline conditions shown in Table 2 and are expected to be typical of the times and temperatures that would exist for applications to pulverized coal (p.c.) fired boilers. The optimum NO_x reduction occurred when the reburning zone was fuel-rich at an overall stoichiometry of 0.9. For high levels of primary NO_x, 630 ppm, the exhaust level of NO was reduced to 200 and 250 ppm for propane and coal as reburning fuels, respectively. For low levels of primary NO the reduction levels were not as significant, dropping from 190 ppm to 100 ppm for propane reburning and only to 180 ppm for coal. The effectiveness of propane over p.c. as a reburning fuel can be attributed to the fuel nitrogen difference. As propane was doped with ammonia to the same nitrogen content of the coal, similar NO_x levels were produced.

A wide variety of reburning fuels were investigated including hydrocarbon and nonhydrocarbon gaseous fuels and coals of varying rank and nitrogen content. The properties of these fuels are supplied in Table 3. A comparison of the effectiveness of different reburning fuels, drawn from Figure 3, indicates that most fuels are similar. The nonhydrocarbon fuels are generally less effective than those containing hydrocarbons (particularly at longer reburning zone residence times). The Yallourn brown coal was the most effective reburning coal chiefly due to its low fuel nitrogen content and high volatility, and there was a general decrease in effectiveness with fuel nitrogen. Some problems were encountered under fuel-rich conditions to complete the burnout of lower volatile coals such as anthracite and the low-volatile Rosa coal; however, similar reduction levels were achieved under fuel-lean conditions where burnout was adequate.

The predominant effect of fuel type was found to be the nitrogen content of the reburning fuel. The detrimental effect of the nitrogen becomes more apparent at the lower levels of primary NO. As shown in Figure 4 at high primary NO levels, the level of reduction achievable by all reburning fuels tested was similar at the optimum stoichiometry and was in the range of 60-70 percent reduction. It is more difficult to achieve the same reduction at lower levels of NO_x with any fuel type; however, fuels containing fuel nitrogen exacerbate the limitation. Below an initial level of 200 ppm of NO, gaseous fuels containing no fuel nitrogen are required to achieve an overall reduction by reburning.

These studies have indicated that NO_x reduction by reburning is a kinetically controlled process with features similar to the staged combustion processes that have been extensively investigated. In the rich reburning zone the temperature, reaction time, and reactant concentration, all influence the ultimate reduction of NO that can be achieved. The data presented above was at the baseline reburning conditions of T_1 (at the entrance of the reburning zone) of 1700 K (2600°F) and a total reburning zone residence time of 400 msec. The effectiveness of the process is increased at longer residence times as shown in Figure 5 in the range of 140 to 750 msec in the rich zones for all hydrocarbon fuels; nonhydrocarbon fuels (H_2 and CO) had no residence time effects. Detailed species analysis within the reburning zone has indicated that the mechanisms suggested by Glass and Wendt (6) for the rich postflame decay of nitrogenous species are consistent with these results. Although the effectiveness of all coals tested increased with residence time, the magnitude of changes were coal dependent. The bituminous coals demonstrated the largest effect of time similar to gaseous hydrocarbon, while the lower ranked lignite and brown coals were less influenced by residence time.

The influence of the reburning zone temperature was also dependent on the reburning fuel type (Figure 6). As the entrance temperature to the reburning zone was increased from 1700 K to 1833 K (2600°F to 2840°F) the exhaust NO_x levels decreased for all reburning fuels. The largest effect occurred for gaseous fuels, while the impact with pulverized coal was less dramatic. These data suggest placing the reburning jets as close to the main burner zone as is feasible to increase the temperature, and having as large a reburning zone as possible by separating the air injectors away from the reburning fuel jets.

RESULTS--SO_x STUDIES

The primary objective of the sorbent injection studies was to determine the sulfur capture that could be achieved for conditions that were optimal for NO_x control by reburning. As indicated in the previous section, these conditions were a reburning zone stoichiometry of 0.9 and high temperature and long residence times in the reburning zone. The baseline conditions for the sorbent studies are also provided in Table 2. The baseline sorbent chosen was a high-purity calcitic limestone with a trade name of Vicron 45-3. This sorbent has been investigated extensively in other EPA programs.

In Table 4, a list of the sorbents investigated in this study and their properties is presented. The sorbents, all calcium containing materials, include limestones, dolomitic limestones, and hydrates of limestones. The primary differences between these sorbents are the presence of magnesium, whether or not they are hydrates and particle size.

The sorbents were injected either with the reburning fuel or at the same location as the burnout air. In Figure 7 is shown the sulfur capture when the Vicron sorbent was injected in these locations as a function of stoichiometry in the reburning zone. Capture is relatively insensitive to stoichiometry and the differences that do occur can be attributed to slight differences in the furnace temperature profiles (Figure 7b). Significantly better captures were observed for injection in the burnout zones. The reburning zone is significantly hotter than the burnout zone, resulting in less reactive stones (7). Specific surface area measurements were made for sorbents injected into the furnace without SO_2 present. These data indicate a direct (inverse) dependence of specific surface area, and therefore reactivity, with injection and calcination temperature (Figure 8).

The other sorbents have a similar dependence on injection location (Figure 9). In every case, injection with the burnout air was preferred with capture increasing with calcium/sulfur ratio. Dolomite was the most reactive sorbent tested in these experiments. However, more dolomite by weight must be added to achieve the same Ca/S ratio due to the Mg component. The capture difference between sorbents and injection temperatures was found to be directly related to the specific surface area after calcination (see Figure 8). The higher surface areas of dolomite are likely due to presence of the magnesium which prevents the calcium oxide particles from recrystallizing into closed forms with low surface area. The causes for the higher surface area of hydroxides are uncertain but may be due to a transition crystal state.

The results presented above are for gas reburning and sorbent injection. When coal was used as the reburning fuel, the results were similar but somewhat increased over the gas results (Figure 10). These improved capture levels cannot be attributed to changes in furnace temperature profiles since only slight changes were measured. The discrepancy is likely due to mineral matter interaction which can enhance sorbent reactivity (8).

SUMMARY AND CONCLUSIONS

The process chemistry of the reburning/sorbent injection technology has been examined in some detail. NO_x reduction by reburning has been found to be similar to staged combustion processes. The influence of individual parameters for each zone of the process on the effectiveness of the NO_x control achieved has been examined. Table 5 presents a summary of the determined influences of these process variables. The impact refers to the direct effect on the chemistry of the process. Under conditions of actual applications, there were a number of secondary influences which will influence the actual level of NO_x achieved. For example, to maintain total load, the firing rate to the main combustion zone will be lowered by an amount corresponding to the reburning fuel addition. This reduction in load can have a variety of effects (both positive and negative) on the NO level exiting this zone and therefore the exhaust emission of NO_x.

When combined with sorbent injection, the reburning process has the potential for simultaneous NO_x/SO_x control. Sulfur capture by calcium containing materials is very sorbent- and temperature-dependent. The important process variables are also provided in Table 5. The highest sulfur captures were achieved with dolomitic sorbents injected at lower temperatures; e.g., with burnout air. The dominant physical parameter of the sorbent is the specific surface area after calcination. Specific surface area appeared to directly correlate with capture for the sorbents and injection locations investigated in this study. However, it is uncertain what determines the specific surface area of different sorbents.

These studies have concentrated on the chemistry of the reburning/sorbent injection process under ideal conditions; i.e., rapid mixing and distinct zones. Activity is now underway to investigate the impact of scale and finite rate mixing. These tests are being carried out at a firing rate of 3 MW (10×10^6 Btu/hr).

ACKNOWLEDGEMENTS

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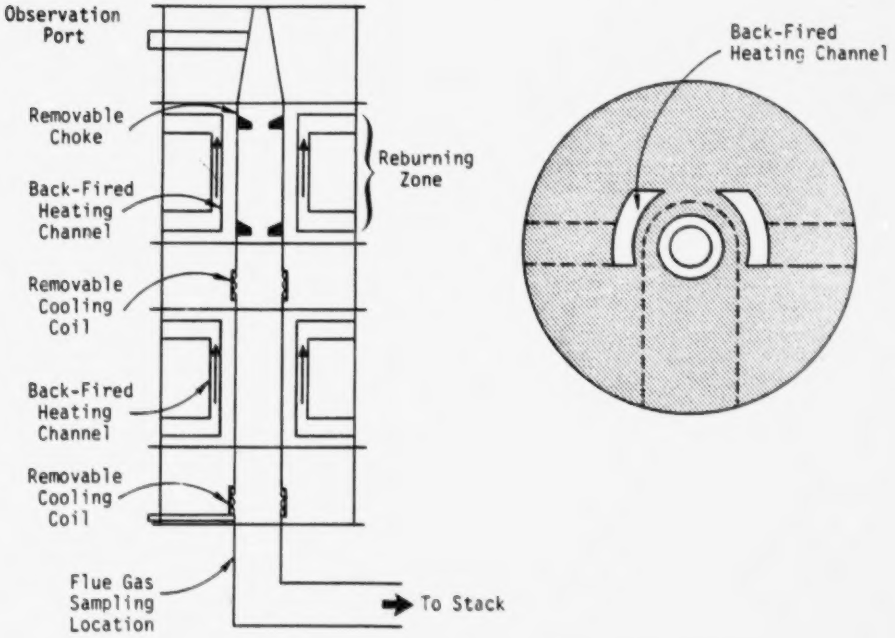
Observation Port
Removable Choke
Back-Fired Heating Channel
Removable Cooling Coil
Back-Fired Heating Channel
Removable Cooling Coil
Flue Gas Sampling Location
Reburning Zone
To Stack
Back-Fired Heating Channel

Figure 1. Cross-sectional views of the control temperature tower.

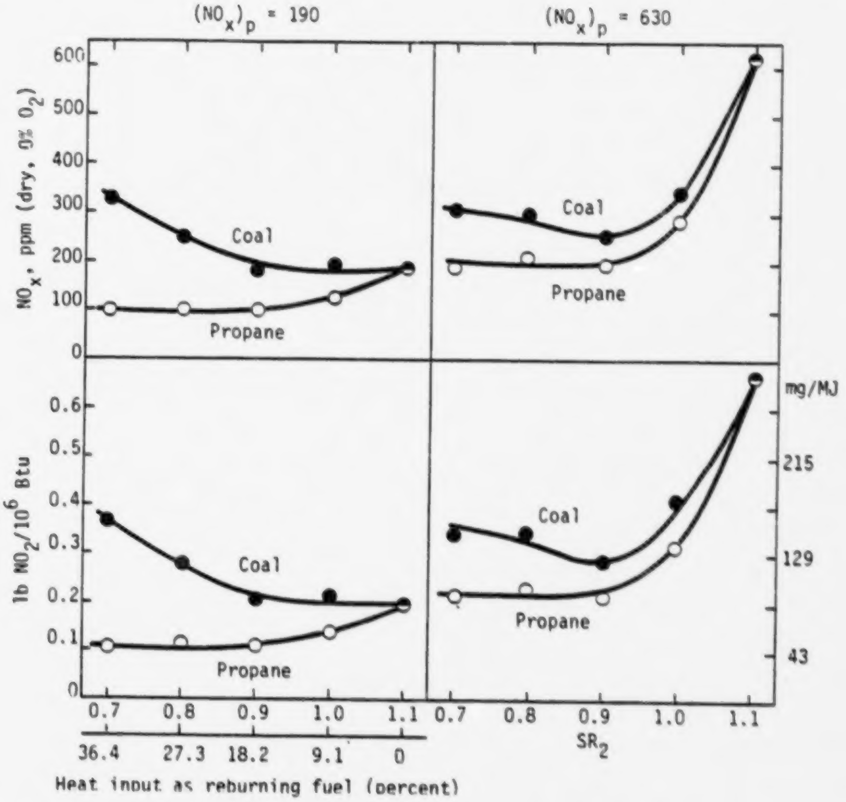

Figure 2. Influence of process parameters on reburning effectiveness.

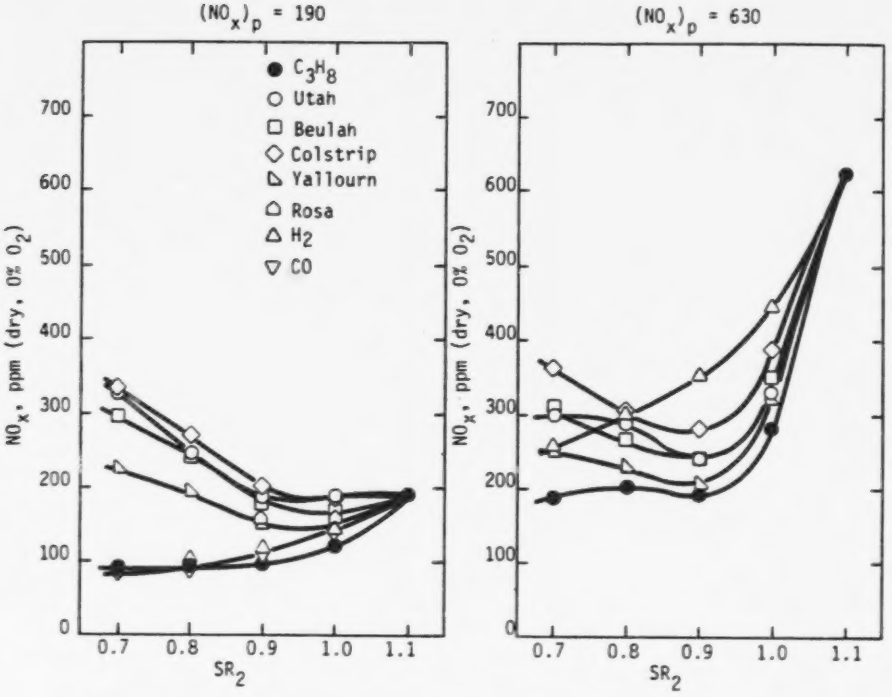

Figure 3. Comparison of different reburning fuels.

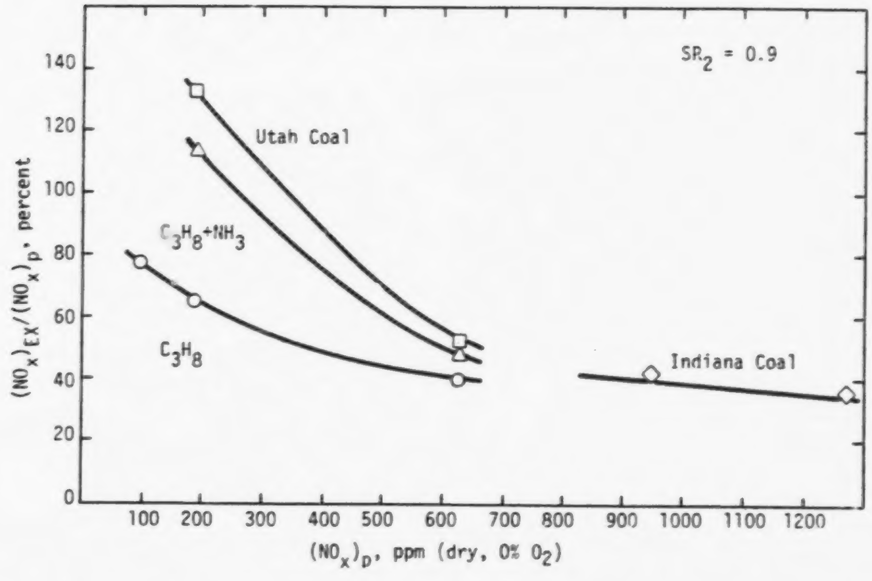

Figure 4. Impact of primary NO$_x$ on effectiveness of reburning.

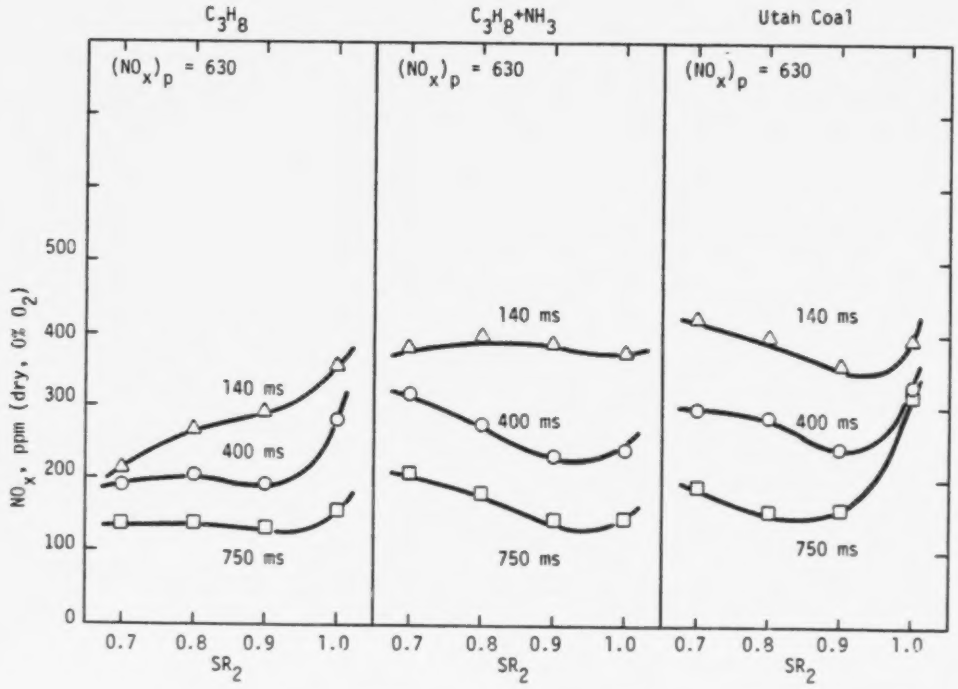

Figure 5. Influence of residence time.

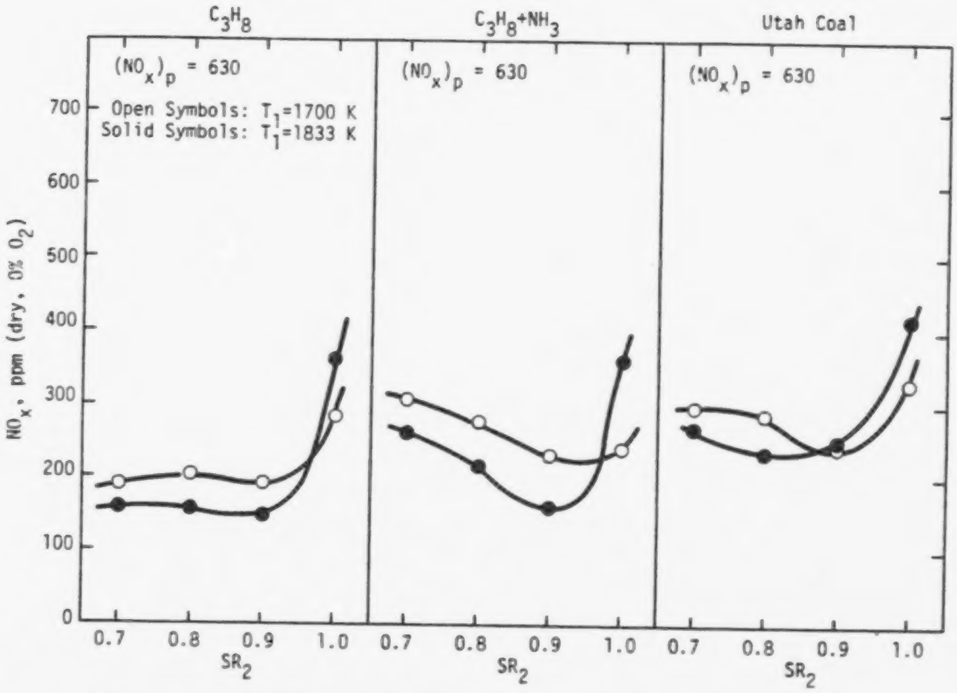

Figure 6. Influence of reburning zone temperature.

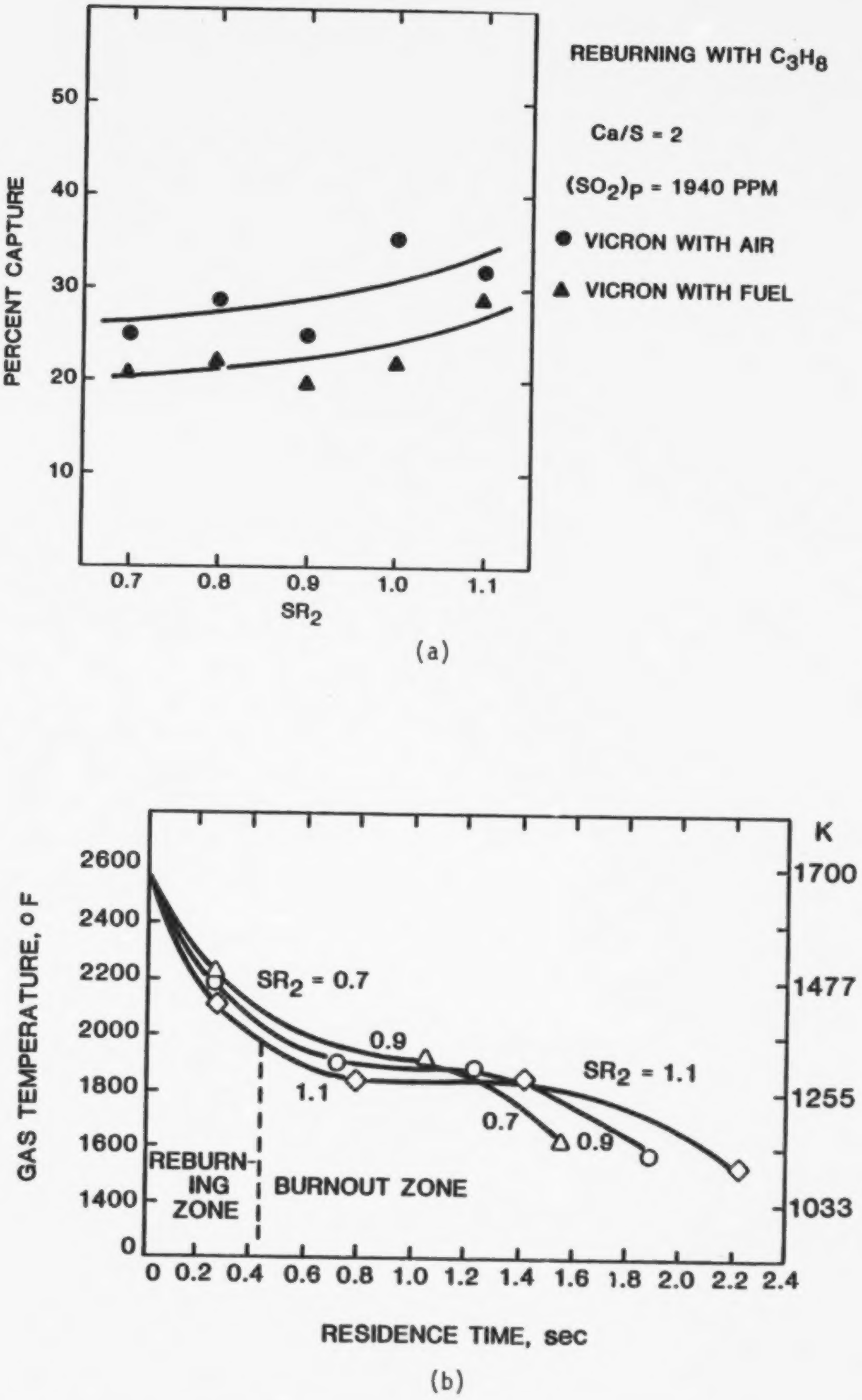

Figure 7. Sorbent injection--impact of injection location and furnace characteristics on sulfur capture for reburning conditions.

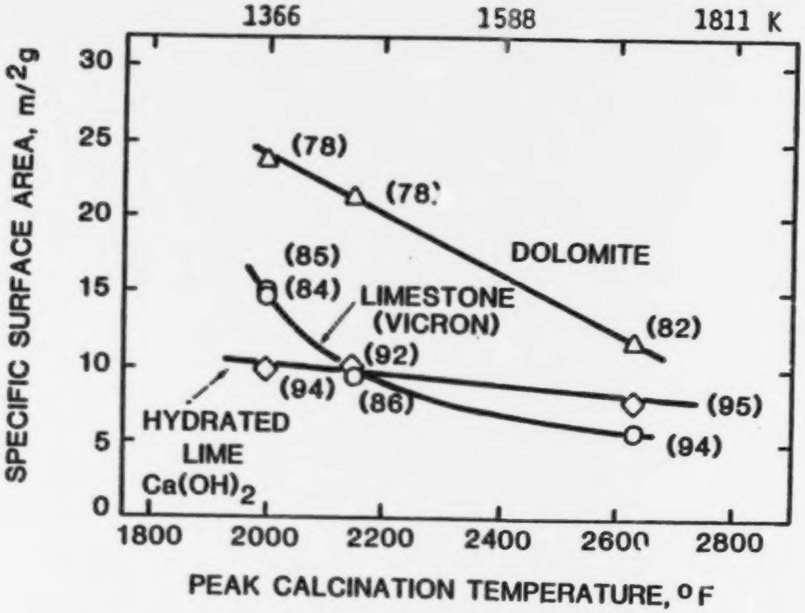

Figure 8. Sorbent injection--sorbent type. Impact of injection temperature on specific surface area without sulfur present for three sorbents. Numbers in parenthesis are extents of calcination after approximately 0.5 sec.

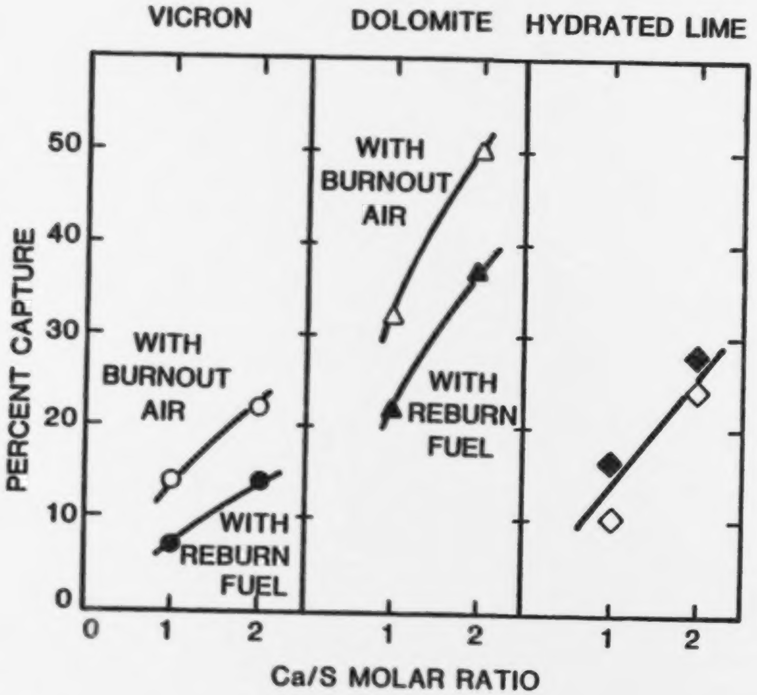

Figure 9. Impact of injection location, sorbent type, and Ca/S ratio on sulfur capture under reburning conditions (C_3H_8 reburning, $SR_2 = 0.9$).

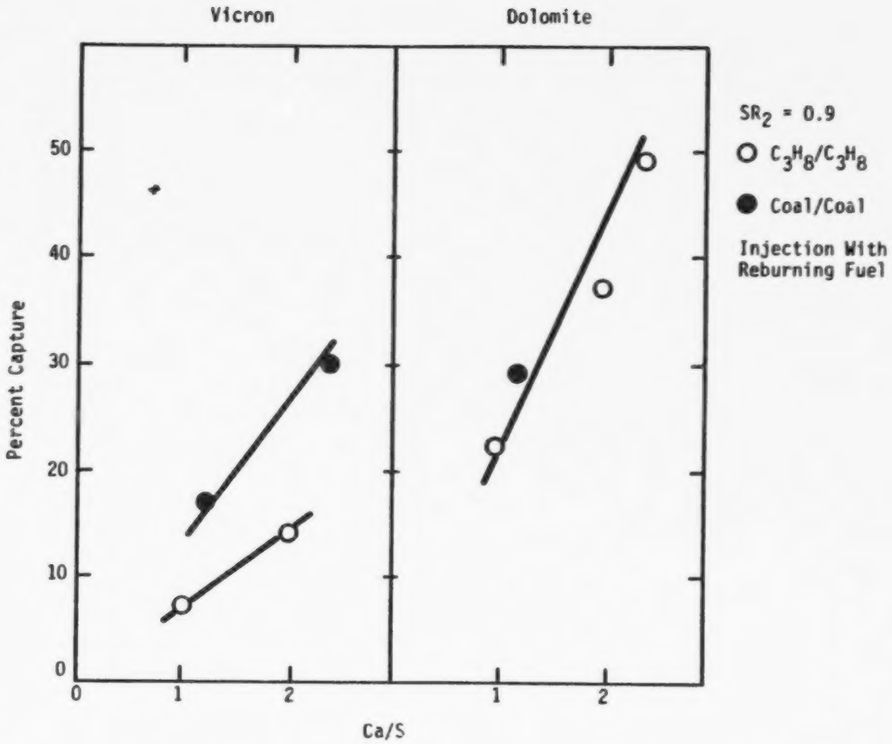

Figure 10. Comparison of coal versus gas for sulfur capture when sorbent is injected with the reburning fuel.

Table 1

CONTINUOUS GAS ANALYSIS INSTRUMENTS

Gas Measured	Detection Principle	Manufacturer	Model No.	Range
NO, NO_2	Chemiluminescent	Thermo Electron Corp. (TECO)	10 AR	0-1000 ppm
CO	Nondispersive Infrared (NDIR)	Anarad, Inc.	AR500R	0-500 ppm
CO_2	Nondispersive Infrared (NDIR)	Anarad, Inc.	AR500R	0-25%
O_2	Paramagnetic	Taylor Servomex	OA-272	0-10%
SO_2	Nondispersive Ultraviolet (NDUV)	DuPont	400	0-5000 ppm
H_xC_y	Flame Ionization (Heated)	Beckman Instruments, Inc.	402	500 ppm (C_3H_8)

Table 2

BASELINE OPERATING CONDITIONS

Primary Zone

- Propane fired at 17.6 kW (60 x 10^3 Btu/hr)
- $SR_1 = 1.10$
- $(NO_x)_p = 190$ ppm (dry, 0% O_2)
- $(SO_2)_p = 1940$ ppm

Reburning Zone

- $\tau_2 = 400$ ms
- T_1 (reburning fuel injection temperature) = 1700 K (2600°F) lower auxiliary burners off

Burnout Zone

- $SR_3 = 1.25$
- T_2 (burnout air injection temperature) = 1505 K = (2250°F) lower auxiliary burners off
- Sorbent - Vicron 45-3; Ca/S = 2

Refractory chokes were placed at the reburning fuel and burnout air injection locations (see Figure 1). The chokes separated the zones by preventing any backmixing between the zones. The primary fuel (propane) was doped with NO to the desired concentrations.

Table 3

FUEL ANALYSIS

Fuel / Property	Yallourn, Australia	Beulah, ND	Colstrip, MT	Indiana	Pennsylvania	Rosa, AL	Utah
Rank	Brown	Lig A	Sub B	HVB	Anthracite	MV	HVB
Proximate Analysis (Percent, as received)							
Moisture	13.97	33.10	21.27	4.54	5.13	8.02	6.39
Ash	1.26	7.12	9.58	8.96	5.74	6.79	7.40
Volatile Matter	45.20	28.65	30.82	37.73	4.39	21.81	38.89
Fixed Carbon	39.57	31.13	38.33	48.77	84.74	63.38	47.32
Calorific Value MJ/kg	21.9	16.9	21.3	28.4	30.5	31.2	28.7
Sulfur	0.20	0.76	0.50	1.87	0.44	0.96	0.64
Ultimate Analysis (Percent, dry)							
C	66.03	65.29	67.52	71.17	88.45	81.23	73.17
H	4.55	3.96	4.36	4.75	2.14	4.73	5.55
N	0.55	0.99	1.38	1.44	0.79	1.74	1.54
S	0.23	1.14	0.63	1.96	0.47	1.04	0.66
Ash	1.46	10.64	12.17	9.39	6.05	7.38	7.90
O	27.18	17.98	13.94	11.29	2.10	3.88	11.18

Table 4

SORBENT PROPERTIES

Sorbent	Vicron 45-3	Dolomite	Hydrated Lime
Petrographic Characterization:			
Type	Calcite	Dolomite	Hydrated Lime
Composition	$CaCO_3$	$CaCO_3$+$MgCO_3$	$Ca(OH)_2$
Grain Size, µm	500-700	<100	30
Top Size, µm	40-45		
Mean Size, µm	11-12	34-40	11-12
Bottom Size, µm	0.3-0.8	1.0	0.3
Density, g/cm^3	2.757	2.855	2.350
Oil Absorption	14		
Uncalcined S. A., m^2/g	0.6-0.9	0.6	12.1-13.5
Ignition Weight Loss, % (1000°C)	41.0-44.0	44.2-47.1	25.3
Hydration Weight Gain (1000°C)	33.08	67.5	
Chemical Composition, %			
Ca	39.2	21.0	51.0
Al	0.07	0.09	0.26
Si	0.07	0.37	0.80
Fe	0.037	0.102	0.22
Na	0.022	0.033	
Mg	0.485	12.1	
K	0.011	0.039	0.51
Cr	0.006	0.27	

Table 5

INFLUENCE OF PROCESS VARIABLES ON REBURNING EFFECTIVENESS

Parameter	Impact
Primary Zone	
Stoichiometry	• No effect except will require more reburning fuel for burner operation.
Fuel Type	• No direct effect. Can influence through temperature and NO level entering reburning zone.
NO Level	• Strong effect. More difficult to reduce lower levels of primary NO.
Reburning Zone	
Stoichiometry	• Optimum at overall stoichiometry of 0.9.
Mixing Rate of Reburning Fuel	• Faster mixing preferred.
Fuel Type	• Hydrocarbon fuels more effective; fuel nitrogen content detrimental at lower primary NO level.
Temperature	• Reduction increases with increasing temperature (2400-2900°F).
Residence Time	• Strong impact, increasing with time (100-750 msec).
Transport Media	• Inert (oxygen free) transport media are desirable since less reburning fuel is required to attain optimum stoichiometry.
Burnout Zone	
Excess Air	• Not important except for burnout.
Air Mixing Rate	• Not important.
Temperature	• Not important unless temperature is dropped to 1200 K where selective NH_i-NO reactions can take place to enhance reduction.
Sorbent Injection	
Sorbent Type	• Dolomite → Hydroxide → Limestone.
Injection Location	• Lower reactivity at higher temperatures.
Sorbent Rate	• Capture determined by Ca/S ratio.
Temperature Profile	• Downstream temperature profile influenced capture.

SESSION IV: BURNERS FOR SIMULTANEOUS SO_2/NO_x CONTROL

Chairman, G. Blair Martin, EPA, IERL/RTP

EVALUATION OF LOW-NO_x BURNERS FOR SO_2 CONTROL

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ABSTRACT

Limestone injection with multistage burners, termed "LIMB," was conceived as a process in which sulfur capture by sorbent material injected through burner passages may be combined with conditions which produce low NO_x emissions in staged, pulverized coal flames. The potential for simultaneous NO_x/SO_x control by low-NO_x distributed mixing burners was evaluated in pilot scale research furnaces. Experimental and commercial burner designs, ranging in capacity from 10×10^6 to 100×10^6 Btu/hr, were considered. Sulfur capture by injected sorbents was relatively insensitive to burner design. Sulfur capture with limestone was generally in the range of 35-40 percent at Ca/S = 2, and up to 40-55 percent for hydrated lime. The key factors in SO_2 removal were reactivity of the sorbent and the temperature history to which the sorbent particles were exposed.

INTRODUCTION

The emphasis of U.S. energy industry has been on the expanded use of coal in utility and industrial applications. Because of the characteristics of coal and its combustion, expanded coal use may result in the increase of pollutant emissions, including NO_x and SO_x. The reduction of NO_x, SO_x, and particulate emissions from fossil-fuel-fired boilers has been a major objective for the U.S. EPA and all of the major boiler burner manufacturers for several years. This is evidenced by a number of unrelated concurrent efforts that have been and are being conducted to develop low-NO_x burners. Various EPA programs have demonstrated the principle of staged combustion as a means of controlling NO_x emissions from coal-fired combustion systems, and have defined design guidelines for the Distributed Mixing Burner (DMB) concept as a viable control technology for new and retrofit applications.

For the last several years EER has been working with the EPA on the development of a low-NO_x pulverized coal burner for wall-fired applications. This DMB consists of a circular burner surrounded by outboard tertiary air ports. The DMB concept involves staging the combustion process to minimize NO_x emissions while maintaining an overall oxidizing atmosphere in the furnace so as to have minimal impact on furnace slagging and corrosion. NO_x production from fuel nitrogen compounds is minimized by driving a majority of the compounds into the gas phase under fuel-rich conditions and providing a stoichiometry/temperature history which maximizes the decay of the evolved nitrogen compounds to N_2 (1). Thermal

NO_x production is also minimized from the fuel-rich zone because of the reduced temperature in a low-NO_x burner.

"LIMB," Limestone Injection with Multistage Burners, was coined to describe the potential simultaneous NO_x/SO_x control using limestone injection with a DMB. It was originally thought that the conditions by which NO_x emissions were reduced with the DMB concept might also enhance the capture of sulfur species with calcium-based sorbents. The lower temperatures within the low-NO_x DMB flame were expected to reduce the degree of deactivation of sorbent materials and thus enhance sorbent reactivity. Injection in the burner would also allow for improved dispersion and mixing of the sorbent particles in the furnace.

This paper summarizes results from an ongoing series of EPA-sponsored investigations designed to develop and evaluate low-NO_x burner designs for combined NO_x/SO_x control with sorbent injection. The burners evaluated included commercial second-generation low-NO_x burners and commercial pre-New Source Performance Standard (NSPS) burners, as well as experimental configurations, at firing rates up to 100 x 10^6 Btu/hr. These different burner designs provided a comparative evaluation of commercial burners in the test furnaces with field operation. The tests, which were conducted in pilot scale facilities at EER, evaluated effects of burner design and operation, fuel type, sorbent type, and sorbent injection configuration. Although a large portion of the work conducted to date has been related to the characterization of NO_x emissions, this paper will be concerned exclusively with SO_2 reduction by sorbent injection in, or close to, the burner.

EXPERIMENTAL SYSTEMS

Test Burners

The potential for SO_2 reduction with sorbent injection has been evaluated for the burner designs listed in Table 1. The burners included several externally staged designs, with tertiary air ports located outside the burner exit, a commercial internally staged burner, and a commercial pre-NSPS burner. The experimental DMB designs, based on EPA DMB design criteria (2) and fabricated for EPA Contract 68-02-2667, utilized generic burner hardware to provide flexibility in operation. The two designs of the prototype DMB for application to industrial boilers, evaluated under EPA Contract 68-02-3127, incorporated Foster Wheeler commercial burner hardware. One of the designs, prototype DMB II, utilized a proprietary Foster Wheeler exit geometry in conjunction with tertiary air ports, while the geometry of prototype DMB III was based on EPA design criteria. The two Steinmuller Staged Mixing (SM) burner designs, evaluated under EPA Contract 68-02-3916, included the SM burner design in operation at Weiher Unit 3, to provide a basis for extrapolating the research furnace test results to an operating boiler, and the modified SM II burner, that incorporated advanced design concepts. Two commercially available Riley Stoker (RSC) burners were evaluated at two firing capacities to establish the performance characteristics in the test facility with which to compare the performance of the RSC DMB to an operating utility boiler as part of EPA Contract 68-02-3913.

The design and performance characteristics of the burners are unique to each manufacturer. The experimental DMBs are all equipped with two parallel secondary air passages with individual swirl and flow control, outboard tertiary air ports, and a central coal passage with a center body, impeller type coal spreader. The industrial prototype DMBs and the RSC DMB also have two parallel secondary air passages and tertiary air ports, but the industrial prototype DMBs utilize the tangential inlet, annular coal passage characteristic of Foster Wheeler equipment while the RSC DMB uses a central coal passage with a venturi nozzle tip and center body impeller. The two Steinmuller SM burners have only one secondary air passage and incorporate an annular coal nozzle much like the Foster Wheeler design. Both annular coal nozzle designs have a large-diameter central passage which accommodates an igniter as well as producing a bluff body recirculation zone to help stabilize the flame. The two commercial Riley Stoker designs have single registers with the difference between the two being the coal nozzle and impeller designs. The RSC Controlled Combustion Venturi (CCV) burner was also equipped with tertiary air ports to permit evaluation of the burner under staged conditions. In the discussion of experimental results, commercial burners are designated by letter code rather than by name.

Research Furnaces

Testing has been conducted in the following research furnaces:

- Large Watertube Simulator (LWS)
- Medium Tunnel (MT)
- Small Watertube Simulator (SWS)

The LWS, shown in Figure 1, was designed to simulate the geometry of a small front-wall-fired boiler, with a hopper bottom and a nose above the firing zone. The furnace sidewalls are partially insulated with refractory. The MT and SWS, shown schematically in Figure 2, are both partially insulated, horizontal tunnel furnaces with burners mounted on one end and with the exhaust exiting from the opposite end. The LWS and MT are both cooled externally with water spray while the SWS is cooled with a water jacket. Nominal firing rates for these furnaces are 100×10^6, 50×10^6, and 10×10^6 Btu/hr for the LWS, MT, and SWS, respectively.

Fuels and Sorbents

A wide range of coals and sorbents have been evaluated in these pilot scale burner tests. A total of nine different coals have been tested with sulfur content ranging from 0.72 to 3.97 percent on a dry basis. The principal coals of interest, listed in Table 2, are all high-volatile bituminous coals. Utah coal, a high-volatile B bituminous with nominally 0.75 percent sulfur content, is used at EER as a baseline coal.

The sorbents used have been calcium-based materials, including limestone, hydrated lime, dolomite, and pressure-hydrated dolomitic lime. Typical sorbent characteristics are listed in Table 3. The baseline sorbent is Vicron 45-3, a pulverized high-purity limestone chosen because of the exceptional quality control which ensured repeatability among batches.

RESULTS

Burner Tests in Large Watertube Simulator

The sulfur reduction potentials achieved by burners tested in the LWS with Utah and Indiana coals are compared in Figures 3 and 4. The data shown were obtained at optimum full-load design point conditions for each burner. The DMB data shown represent data from tests of the 70 x 10^6 Btu/hr industrial prototype DMB III. The other burners were tested at a nominal 100 x 10^6 Btu/hr. The limestone material was injected both with the coal and through nozzles located on the axis of each tertiary air port. SO_2 capture was highest for the industrial prototype DMB III for both coals and each sorbent/injection location pair. The other consistent trend was that hydrated lime injected through the tertiary air ports produced greater SO_2 reduction than did the limestone material. The SO_2 removal achieved at Ca/S = 2 was in the range of 35-40 percent for the limestone and 40-55 percent for the hydrated lime. None of the 100 x 10^6 Btu/hr burners had a consistent advantage in terms of SO_2 reduction potential.

The effect of firing rate on SO_2 reduction of burners tested in the LWS is shown in Figure 5. Burners C and E, and burners B and G represent scaled pairs of burners. Burners C and B have a design capacity of 100 x 10^6 Btu/hr, while burners E and G are scaled for 50 x 10^6 Btu/hr. Reducing the thermal input from 100 x 10^6 Btu/hr to 50 x 10^6 Btu/hr resulted in an improvement in sulfur capture for burners C and B. Capture for the scaled-down burners, E and G, was better still than the full-scale burners operated at half load. Because of the LWS characteristics, a reduction in load increases mean residence time but also reduces the mean and peak furnace temperatures. The result is that the time available in the sulfation temperature window, 1500-2200°F, is relatively insensitive to load. The aerodynamics of the full-scale burners operated at half load are considerably different than those of a burner designed for reduced loads; thus, interaction of the sorbent particles in the region around the burner also differs.

The effect of coal composition on sulfur capture is shown in Figure 6. The trends for all three fuels were similar, with the highest sulfur capture achieved by injecting hydrated lime through the tertiary air ports, and with little difference in the effectiveness of injection locations with limestone. Intuitively, an effect of composition, sulfur content in particular, would be anticipated. The sulfation reaction would be thought to be driven in part by the concentration of sulfur species. The SO_2 capture data presented, however, show no discernible effect of coal composition.

The effect of sorbent type on SO_2 reduction is shown in Figure 7. The test results are shown for staged conditions with sorbent injected through the tertiary air ports and unstaged conditions with sorbent injected into the coal stream. Dolomite achieved the highest capture for both cases. Overall, these results indicate that dolomite is a better sorbent for comparable Ca/S molar ratios than either limestone or hydrated lime. However, approximately 60 percent more dolomite by weight is required to achieve comparable Ca/S ratios. Such results are also consistent with data obtained in smaller furnaces and laboratory scale equipment.

The effect of sorbent injection velocity is shown in Figure 8. Doubling the velocity of the sorbent when injected through the tertiary air ports as a double concentric jet increased capture from 37 to 44 percent at Ca/S = 2. The higher speed jets are characterized by significantly increased entrainment of hot combustion gases from the flame zone. The sorbent particles may also be ballistically thrown past peak temperature regions of the flame. In either case, sulfur capture was improved.

Thermal Environment and Furnace Characteristics

The two primary processes by which sorbent particles remove gaseous SO_2, sorbent calcination and sulfation, have been shown to be very sensitive to the temperature history experienced by the sorbent particles (3). The reactivity of a given sorbent is strongly dependent on the peak temperature seen by the sorbent particles, and sulfation is determined by the amount of time available in the most favorable temperature regime of approximately 2250-1800°F (4). The thermal characteristics through the sulfation temperature window are shown in Figure 9 for the experimental furnaces of interest to this study. In Figure 10 these temperature profiles have been coupled with a sulfation model to predict overall SO_2 capture for a $CaCO_3$ sorbent of differing reactivity. Sorbent reactivity is dictated by the peak temperature (and time) experienced by the sorbent, and may be characterized by measurable parameters such as specific surface area (3).

The characteristic curves for the LWS furnace indicate that, compared to most boilers, this furnace has a long time available in the sulfation window, and that overall SO_2 capture is not limited by sulfation. In this case SO_2 capture will be determined by the reactivity of the sorbent material, and hence by peak temperature. For the LWS experimental data, the spread in SO_2 capture by the $CaCO_3$ (for different burners, burner parameters, and injection methods) can be explained by differences in peak temperature seen by the sorbent of no more than 200°F. Such temperature differences can easily be achieved by relatively small changes in burner and sorbent injection aerodynamics.

In order to further investigate the impact of furnace thermal environment, limited data are presented for tests in the MT and SWS furnaces. Sulfur captures for a 50×10^6 Btu/hr experimental DMB and the industrial prototype DMB II in the MT furnace are compared in Figure 11. Both burners were fired at a nominal 50×10^6 Btu/hr to fit the confines of the furnace. These data indicate large differences in sulfur capture for injection of limestone with the coal compared with injection through the tertiary air ports. Although capture by sorbent injected with the coal for the industrial prototype DMB II in the MT is comparable to results from the LWS, injection through the tertiary air ports is much lower in the MT. The high firing densities and flame confinement in the MT apparently produced an unfavorable thermal environment for the particles injected through the tertiary ports. The central core of the flame, however, apparently was unaffected by the MT cooling profile and thus yielded sorbent particles whose reactivity was similar to those produced in the LWS.

The effect of furnace cooling on sulfur capture was also evaluated in the SWS, as shown in Figure 12. The thermal environment, designated by the furnace temperatures, was varied by changing the insulation distribution within the furnace. Again, conditions with the lowest bulk temperatures yielded the highest SO_2 removal. In fact, the configuration with an exit temperature of about 2300°F produced an essentially unreactive sorbent.

Extrapolation to Boiler Temperature Profile

Experimental data can be translated into predictions for anticipated boiler SO_2 capture in much the same way that Figure 9 was used in the generation of Figure 10. One example for an assumed boiler temperature profile is presented in Figure 13. This figure shows the effect of injecting a $CaCO_3$ sorbent at different elevations in the boiler. When sorbent is injected near the burner zone, the peak temperatures experienced limit sorbent reactivity and hence overall SO_2 removal. As the sorbent injection location is moved to lower temperatures at higher elevations, reactivity and SO_2 capture improve. Ultimately there is a trade-off between increased reactivity and reduced residence time in the sulfation temperature window. In the example shown, for the specific boiler and sorbent combination of Figure 13, the optimum injection temperature is between 2100 and 2200°F.

This example is consistent with the experimental furnace data, and would suggest that for conventional sorbents there is little advantage to sorbent injection in the burner zone, and that upper furnace injection is to be preferred. Moreover, the reactivity vs. temperature characteristics of normal limestone materials are such that high SO_2 removal levels are not expected. High SO_2 capture can, however, be achieved with very reactive sorbent materials, even in adverse temperature fields. An example is shown in Figure 14 for the SWS furnace operating with a temperature gradient not atypical of many U.S. boilers. This figure illustrates that, as the injection location is moved away from the burner zone to downstream locations, SO_2 removal is improved. Downstream injection of a pressure hydrated dolomite results in greater than 70 percent SO_2 removal at a Ca/S = 2. This particular material is available commercially and has shown consistently good performance in both small and pilot scale tests.

CONCLUSION

The results of these pilot scale tests indicate that burner design has only limited effect on sulfur capture. Capture depends on the interaction of the sorbent with the flame and can be optimized for all burners. However, data indicate that, for limestone at Ca/S = 2, only 35 to 40 percent SO_2 removal can be expected. Hydrated lime, when injected away from the flame zone, can be expected to achieve 40 to 55 percent capture at similar stoichiometry. Differences in SO_2 removal rates in the LWS furnace are consistent with differences of no more than 200°F in the peak temperature experienced by the sorbent.

The experimental data can be rationalized in terms of sorbent reactivity, and by the temperature/time profile through the optimum sulfation temperature window. Both parameters are influenced by sorbent characteristics and by specific furnace thermal environment. A knowledge of both parameters is required to interpolate data between experimental furnaces, and to extrapolate to operating boilers.

By avoiding high temperatures within the flame and exposing the sorbent to a favorable temperature history, sorbent reactivity can be maximized. However, each sorbent material has unique characteristics. Data indicate that the sulfur capture potential of conventional limestone is limited and that other materials are becoming available which offer the potential for high SO_2 removal rates.

ACKNOWLEDGMENTS

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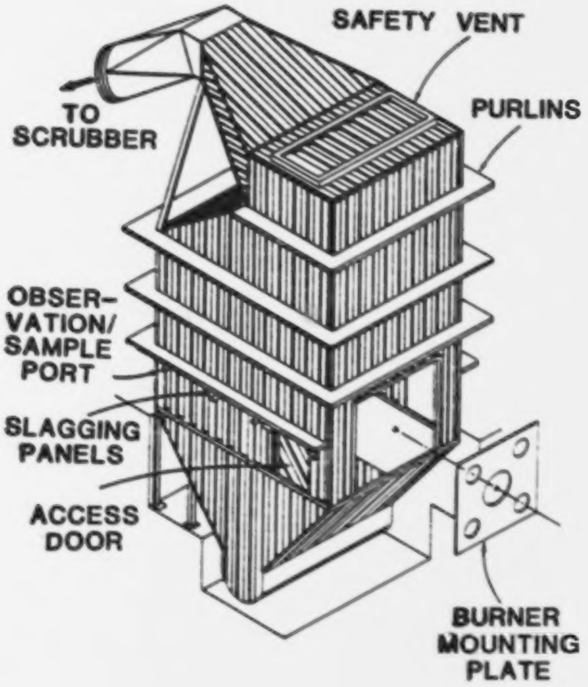

SAFETY VENT
TO SCRUBBER
PURLINS
OBSERVATION/ SAMPLE PORT
SLAGGING PANELS
ACCESS DOOR
BURNER MOUNTING PLATE

FIRING DEPTH
22 FEET

WIDTH
16 FEET

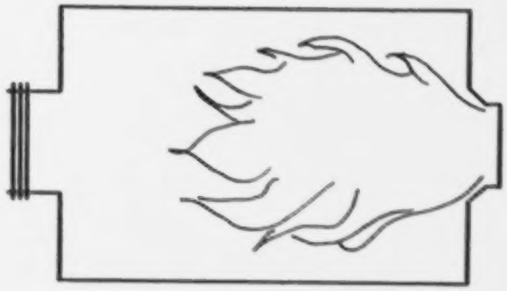
OVERALL HEIGHT
50.5 FEET

WALL FIRED

PARTIAL INSULATION

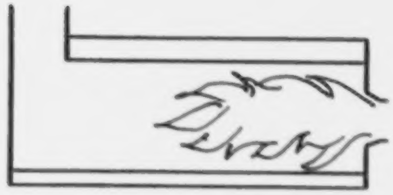
SPRAY COOLED

Figure 1. Large Watertube Simulator Furnace



MEDIUM TUNNEL FURNACE

DIAMETER: 14 Feet
LENGTH: 20 Feet
SPRAY COOLED, PARTIAL
REFRACTORY LINING
50×10^6 Btu/hr Nominal



SMALL WATERTUBE SIMULATOR

DIAMETER: 6 Feet
LENGTH: 17 Feet
WATER JACKET, PARTIAL/VARIABLE
REFRACTORY LINING
10×10^6 Btu/hr Nominal

Figure 2. Schematics of Medium Tunnel and Small Watertube Simulator

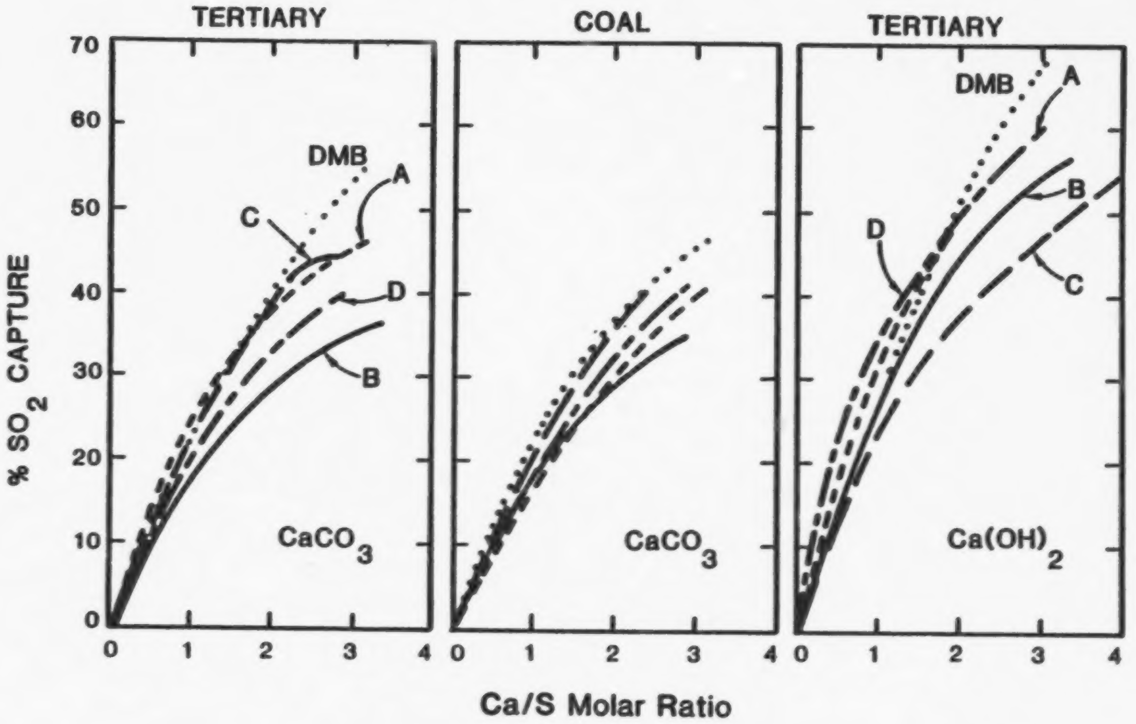


Figure 3. Comparison of Sulfur Capture Potentials for Burners Tested in the LWS with Utah Coal

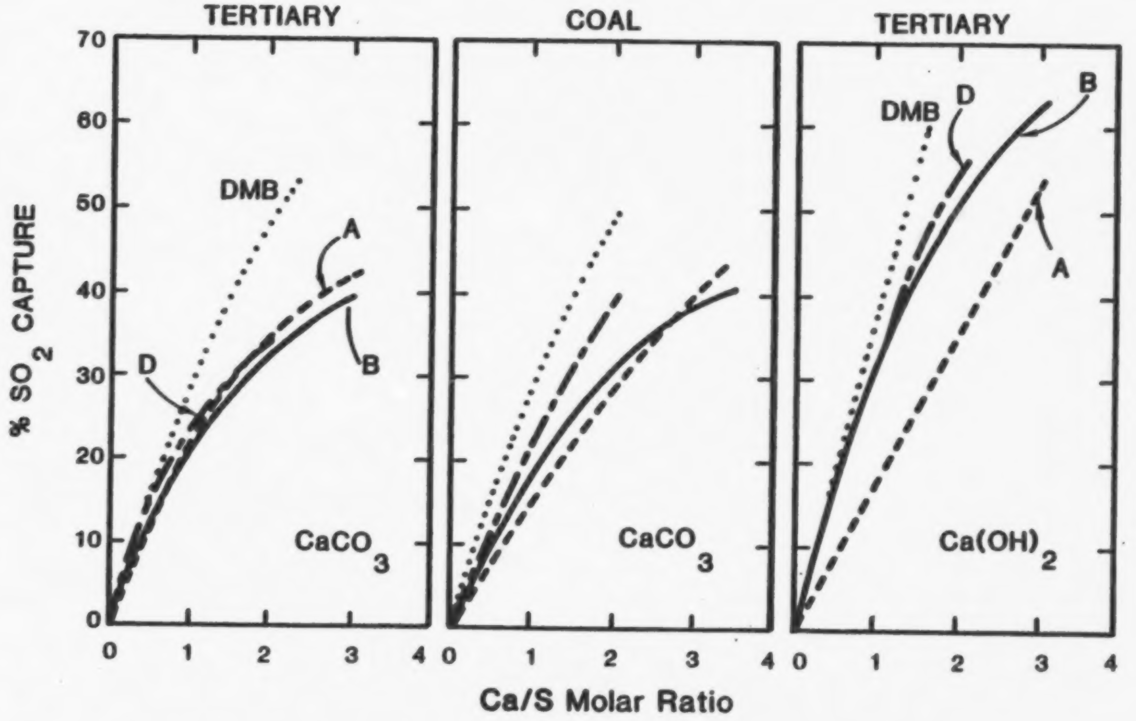


Figure 4. Comparison of Sulfur Capture Potentials for Burners Tested in the LWS with Indiana Coal

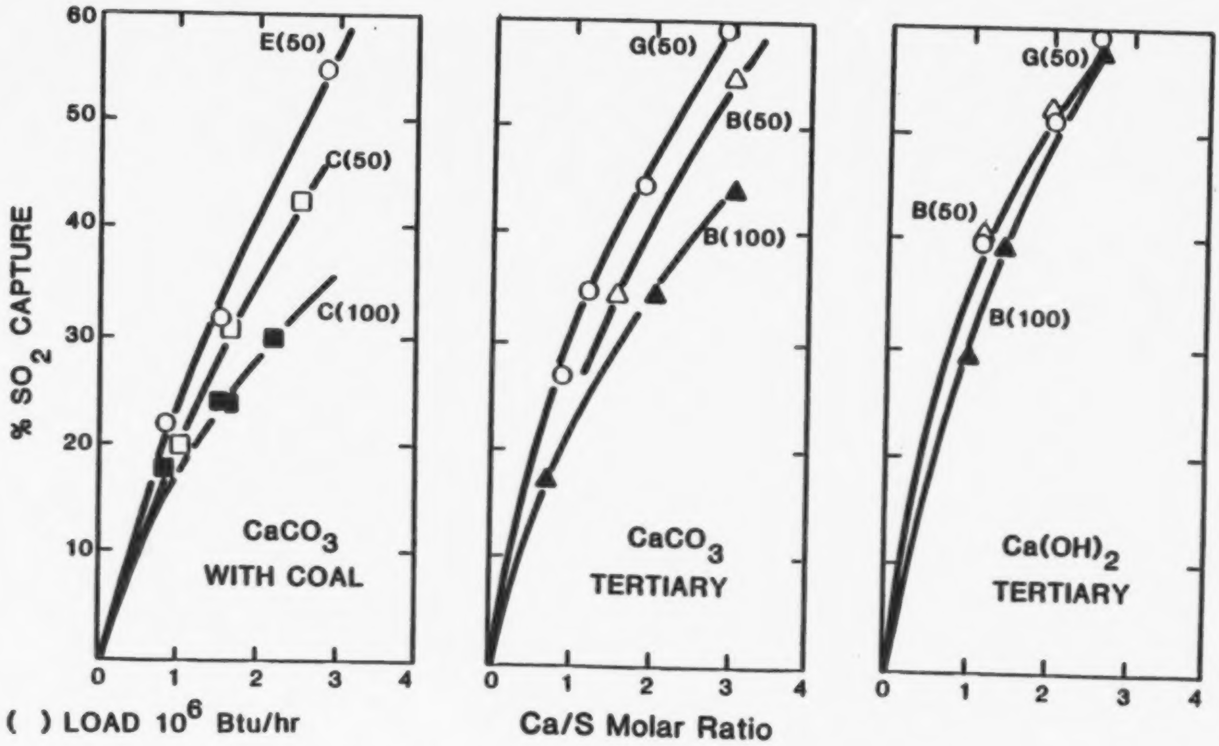


Figure 5. Effect of Firing Rate on SO_2 Reduction

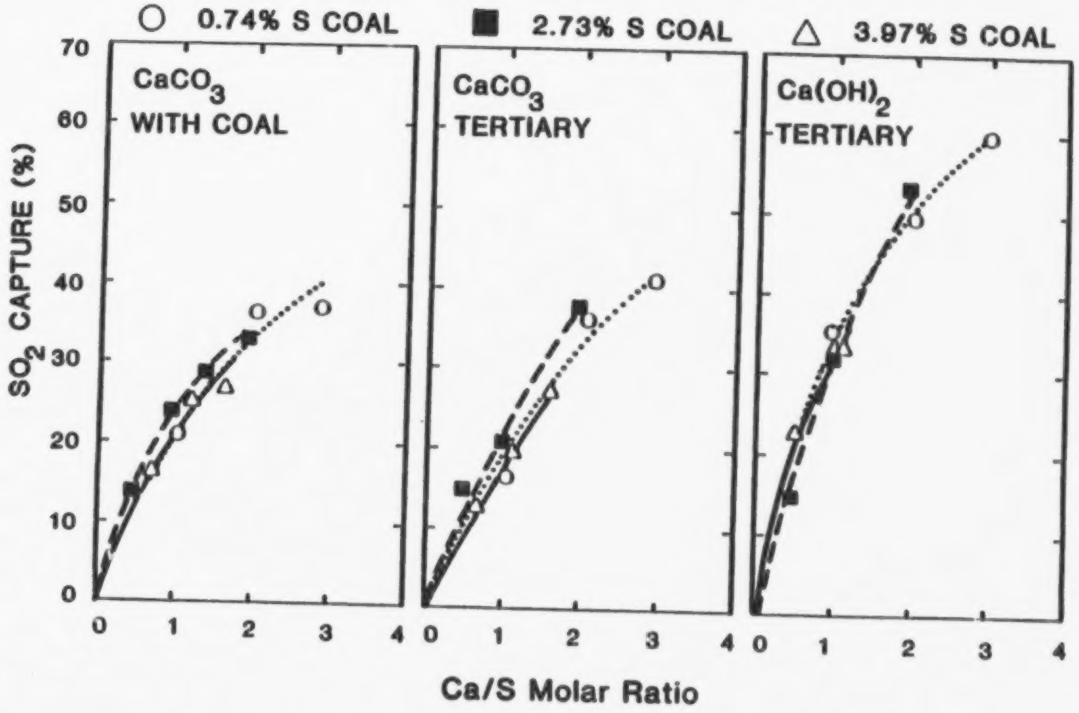


Figure 6. Effect of Coal Composition on SO_2 Reduction with Burner D

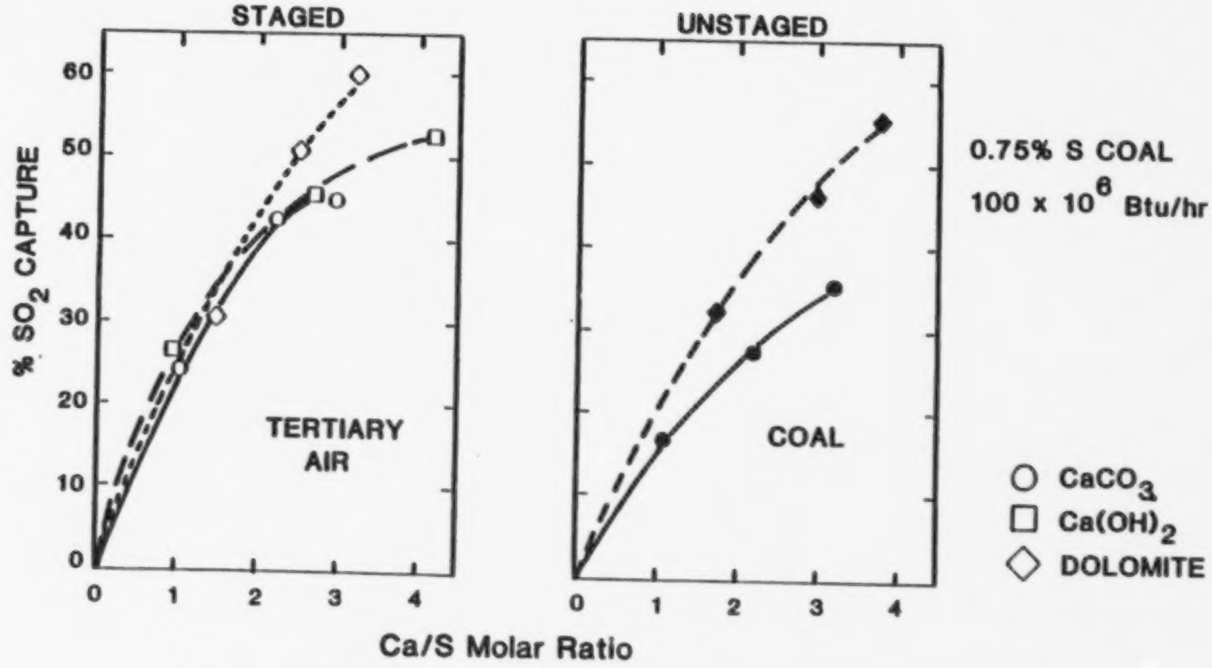


Figure 7. Effect of Sorbent on SO_2 Capture with Burner C

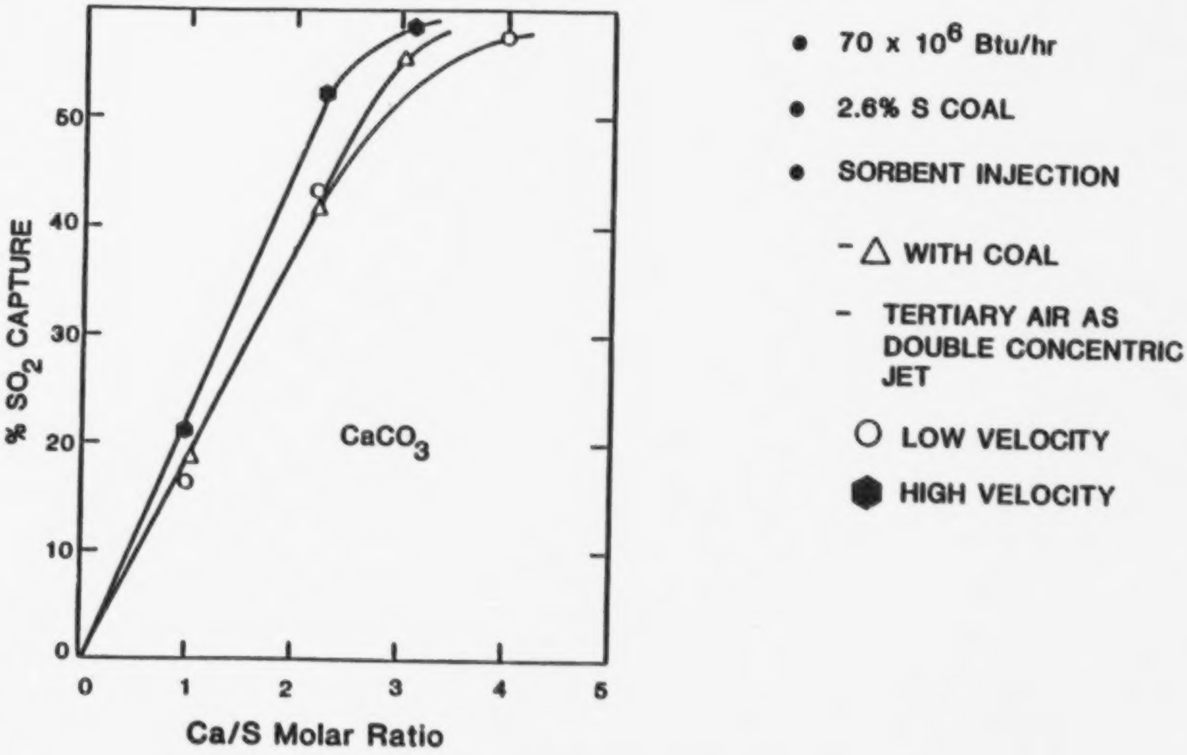


Figure 8. Effect of Sorbent Injection Velocity on SO_2 Capture with Industrial Prototype DMB II

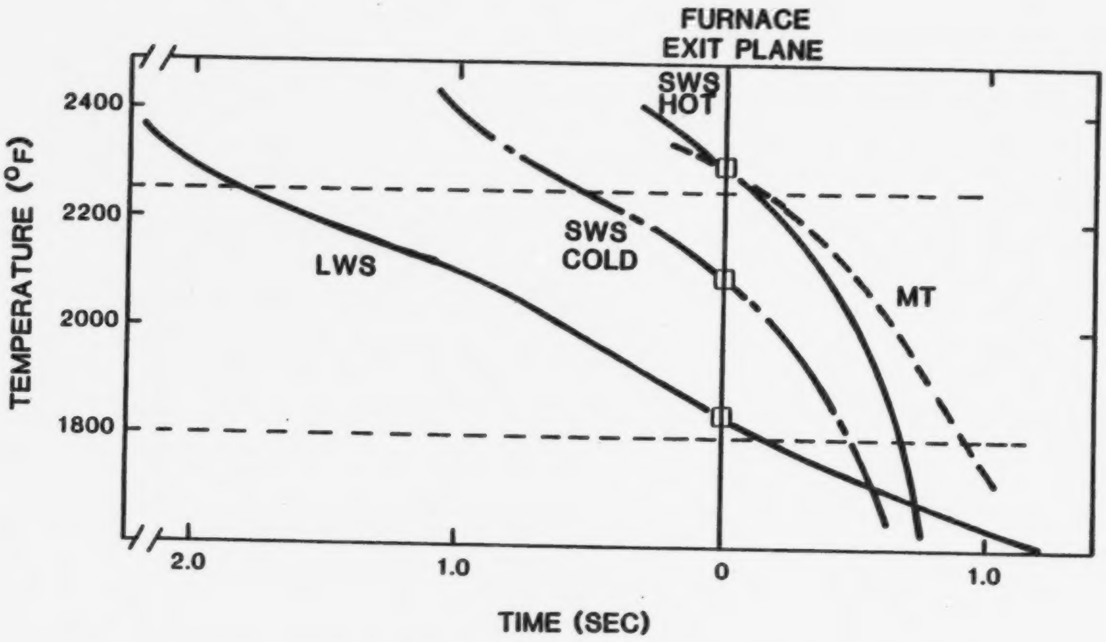
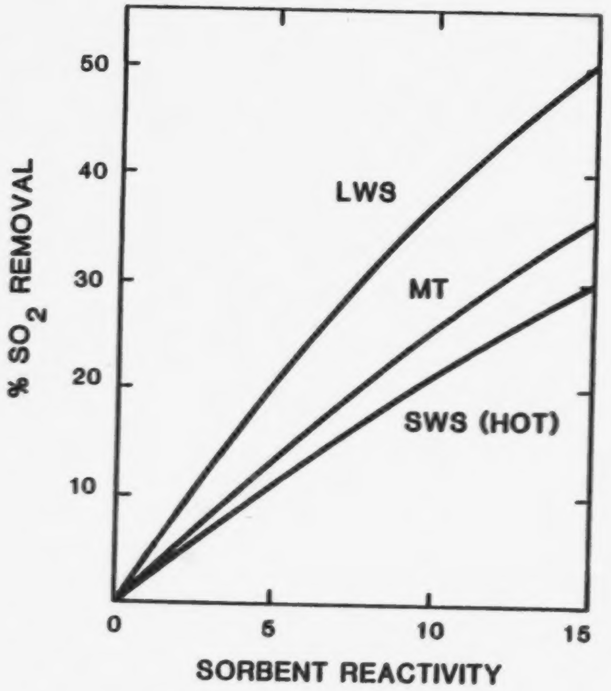


Figure 9. Experimental Furnace Temperature Characteristics at Nominal Load



- **SO_2 REMOVAL VS SORBENT REACTIVITY ($CaCO_3$)**
- **SULFATION MODEL GIVES SO_2 REMOVAL FOR FURNACE dT/dt**
- **REACTIVITY RELATED TO PEAK CALCINATION TEMPERATURE**

Figure 10. Predicted Sorbent Reactivity Based on Furnace Characteristics

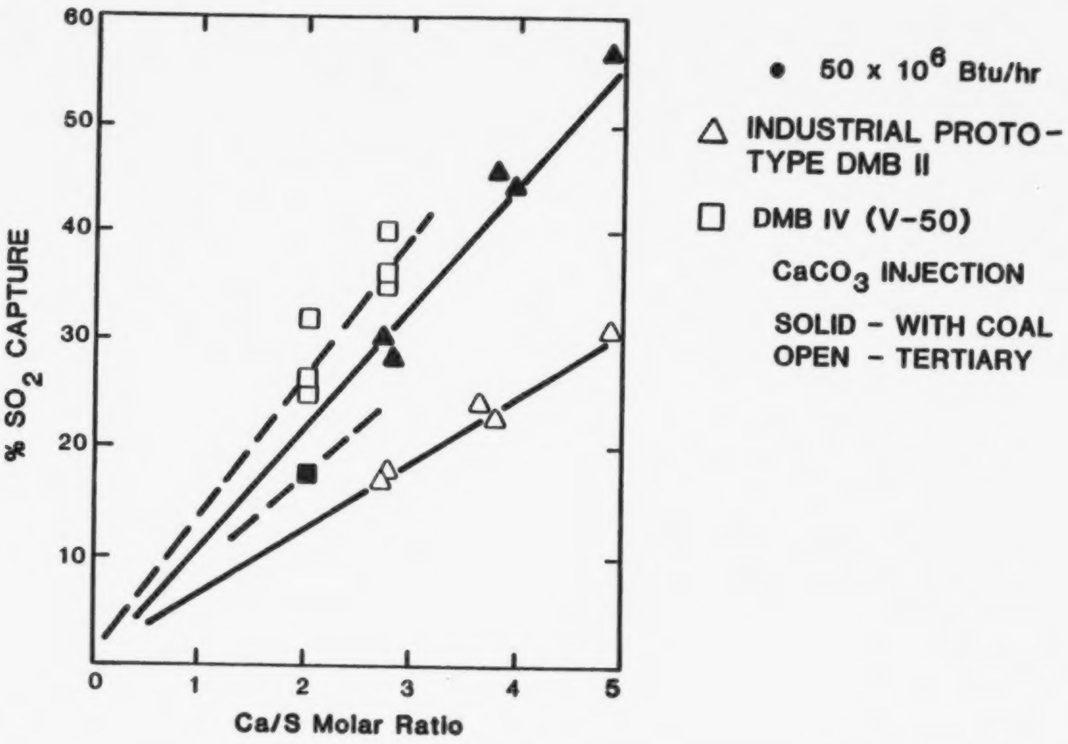


Figure 11. Sulfur Capture with Sorbent Injection in the MT

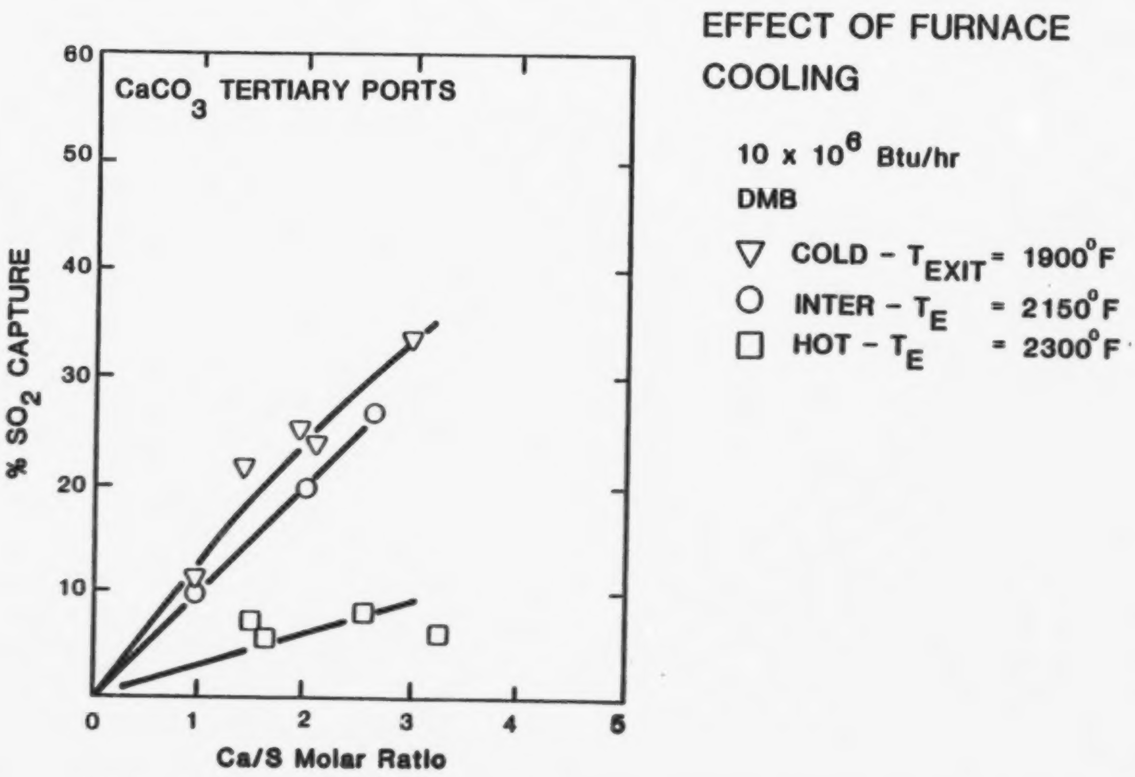
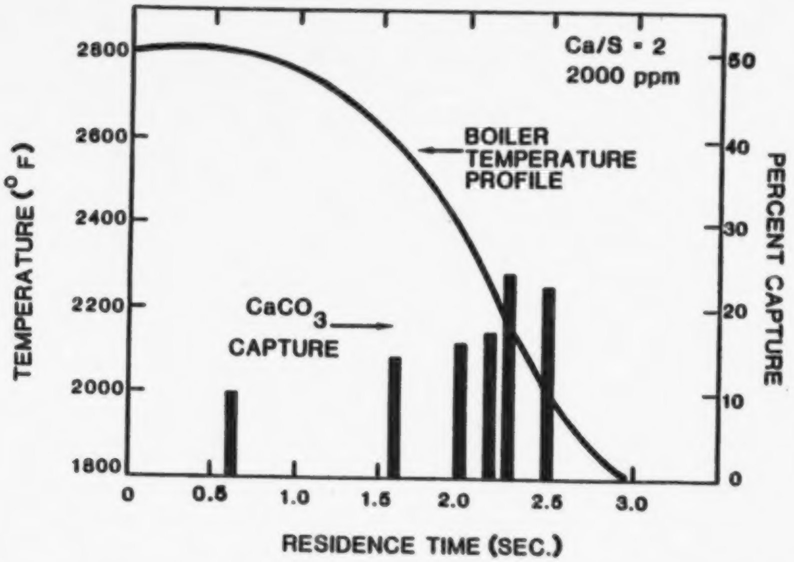


Figure 12. Effect of Furnace Cooling on Sulfur Capture in the SWS



- SO2 CAPTURE VS SORBENT INJECTION AT DIFFERENT BOILER LOCATIONS

Figure 13. Experimental Data Translation to Boiler Temperature Profile

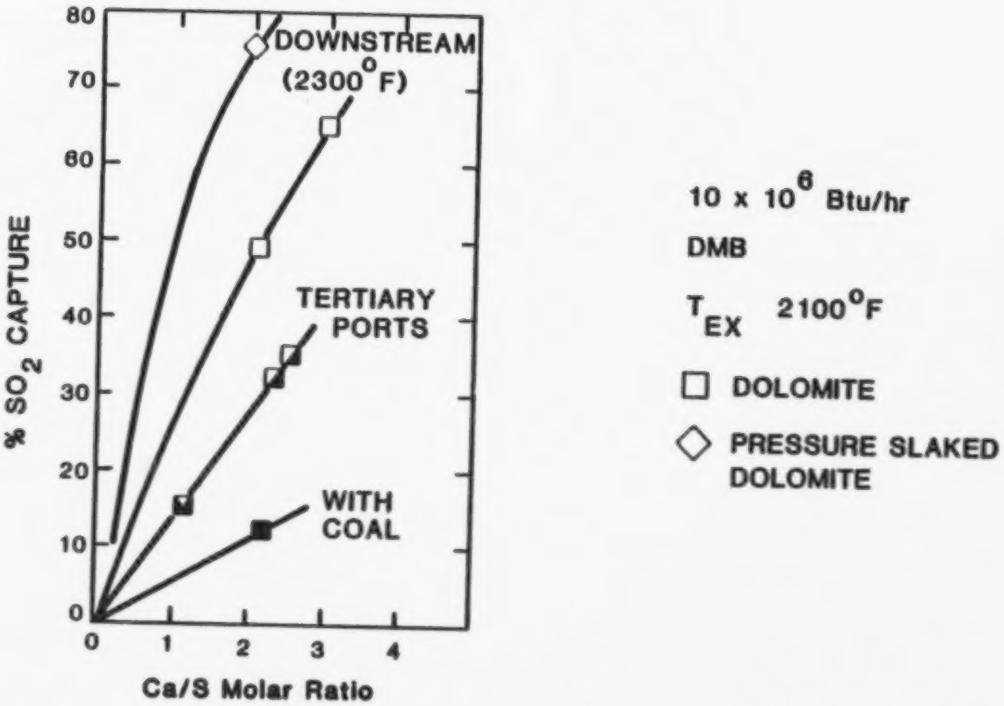


Figure 14. Effect of Sorbent Injection Location on Sulfur Capture in the SWS

Table 1

TEST BURNERS

Burner/Component Manufacturer	Burner	Design	Firing Capacity (10^6 Btu/hr)
Experimental	Modified DMBs	Externally Staged	10, 50, 100
Foster Wheeler	Industrial Prototype DMB II	Externally Staged	70
	Industrial Prototype DMB III	Externally Staged	70
Steinmuller	SM Burner (Weiner)	Externally Staged	50, 100
	SM II Burner	Externally Staged	100
Riley Stoker	RSC DMB	Externally Staged	100
	Controlled Combustion Venturi Burner	Internal and External Staging	50, 100
	Flare Burner	Pre-NSPS	50, 100

Table 2

PRINCIPAL COALS

Coal	Rank	Sulfur Content (Wt %, Dry)
Utah	HVB Bituminous	0.73 - 0.96
Indiana	HVB Bituminous	1.35 - 2.73
Illinois	HVC Bituminous	3.55 - 3.97
Saar (W. Germany)	HVA Bituminous	0.72 - 0.87

Table 3

TYPICAL SORBENT CHARACTERISTICS

Sorbent	Composition	Median Diam. (μm)	Density (g/cm^3)	Chemical Analysis (Wt %)	
				Ca	Mg
Vicron 45-3	$CaCO_3$	9.8	2.71	39.0	0.49
Colton Hydrated Lime	$Ca(OH)_2$	4.0	2.28	51.9	0.25
RWK Hydrated Lime	$Ca(OH)_2$	4.0	2.25	52.9	0.43
Dolomite	$CaCO_3 \cdot MgCO_3$	12.0	2.87	34.7	11.3
Pressure Slaked Dolomitic Lime	$Ca(OH)_2 \cdot Mg(OH)_2$	2.2	2.28	28.6	16.0

LIMESTONE INJECTION WITH AN INTERNALLY STAGED LOW-NO_x BURNER

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ABSTRACT

Foster Wheeler's internally staged, Controlled Flow/Split-Flame low-NO_x burner has been in utility field service since 1979. The ease of retrofit to existing steam generators would make the burner a cost-effective means of implementing the Limestone Injection Multistage Burner concept if satsifactory sulfur capture can be achieved. Two methods of limestone injection internal to the burner are available: pre-mixed with the coal and separate from the coal. The former technique was evaluated in a joint program with the U.S. EPA, while the latter was evaluated independently by Foster Wheeler using a novel injection method. Over 60 percent greater sulfur capture was obtained using the Foster Wheeler technique on a 50 million Btu/hr single burner test furnace.

DEVELOPMENT OF INTERNALLY STAGED
BURNERS FOR LIMB

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ABSTRACT

This paper discusses an experimental investigation directed toward the development of retrofit technology to achieve simultaneous in-furnace control of NO_x and SO_x emissions from coal-fired boilers. Results obtained in a 2.9 MW_t (10×10^6 Btu/hr) test furnace show that NO_x reductions of 50 percent can be obtained from high-velocity pre-NSPS burners by modification of both the coal nozzle and the air distribution without the use of external air ports. The effectiveness of calcium-based sorbent injection for SO_2 control is limited by sorbent reactivity and time/temperature characteristics of the boilers. Experimental results suggest that sorbent injection can be optimized using coaxial air/sorbent jets to achieve maximum sorbent reactivity and dispersion, and thereby optimize SO_2 removal.

INTRODUCTION

Coal-fired electric utility boilers are a major source of NO_x and SO_2 emissions to the atmosphere. These pollutants are considered to be the primary precursers to acid rain. Approximately 85 percent of NO_x emissions and almost all SO_2 emissions from coal-fired utility plants are from boilers constructed prior to 1971, when EPA's New Source Performance Standards (NSPS) for large (greater than 73 MW_t or 250×10^6 Btu/hr) boilers first became effective. In order to control acid rain it is desirable to have cost-effective NO_x and SO_x control technologies which can be implemented on a retrofit basis to existing pre-NSPS boilers.

The objective of retrofit NO_x/SO_x control technologies should be to maximize the potential emission reduction within the retrofit constraints of specific units or classes of boilers. Many current low-NO_x coal burner technologies capable of meeting NSPS NO_x emission limits utilize external (staging or tertiary) air ports or reduced secondary air velocity (enlarged burner throat diameter) to effectively delay fuel/air mixing. For many existing boilers, however, it may be impractical to enlarge the burner throat or install external air ports on a retrofit basis due to structural or other considerations. Thus there is a need to determine the extent to which NO_x emissions can be reduced as a function of

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the range of retrofit constraints imposed by pre-NSPS boiler designs. The parallel application of dry sorbent injection into the boiler furnace for reduction of SO_x emissions offers the potential for significantly reducing the emission of acid rain precursers.

This program is directed toward the investigation of internally staged low-NO_x coal burners for wall-fired boilers, and the utilization of calcium based sorbent injection for SO_x control. The process by which SO_2 is captured by calcium based sorbents has been described in other work (1, 2). Key to the success of the combined NO_x/SO_x control concept is to provide the sorbent with the optimum conditions for maximizing reactivity, achieving good dispersion into the combustion products, and providing adequate residence time within the optimum temperature range (900-1200°C) for SO_2 capture to occur (2,3). Experimental studies are currently underway in 3 MW_t (10×10^6 Btu/hr) and 29 MW_t (100×10^6 Btu/hr) facilities to investigate combined NO_x/SO_x control via application of internally staged burners with sorbent injection. Specific goals of these investigations are to determine the impact of burner design parameters on the level of NO_x control achievable without the use of air ports external to the burner throat, particularly under conditions typical of pre-NSPS boilers. Recent evidence suggests that sorbent injection near the burner is not the most attractive means for achieving high SO_2 captures. Therefore, emphasis has been placed on sorbent injection in the upper furnace. Experiments under this program have investigated the effect of sorbent injection parameters on SO_2 capture in order to establish guidelines for optimizing sorbent injection methods. This paper presents selected results from these experimental studies conducted in the 3 MW_t (10×10^6 Btu/hr) experimental test furnace.

EXPERIMENTAL

Burners

Tests have been conducted with burners designed to achieve both high and low secondary air velocity at the throat section (Figure 1). The high velocity burner was designed to be representative of typical pre-NSPS burners with a secondary air velocity of approximately 58 m/sec (190 ft/sec). Pre-NSPS burners are typically designed to maximize combustion intensity in the boiler furnace. In many existing boilers it is impractical to perform extensive modifications to the burner throat, and burner modifications are limited to the coal nozzle or to air distribution within the existing burner throat. These tests investigated the potential NO_x reduction achievable by modifications to the coal nozzle without changing the existing burner throat. The effect of adding a baffle to the secondary air passage in order to split the secondary air stream (see Figure 1) was also investigated.

The low velocity burner was designed to produce a secondary air velocity of 24 m/sec (80 ft/sec) and represents a more flexible retrofit situation where throat enlargement to reduce air velocity is possible. Both the high and low velocity burners utilized the same air register which supplied the secondary air through two annular passages at the throat of the burner. Air flow and swirl level through each secondary air passage was independently controlled to investigate the impact of these parameters on NO_x control.

Coal Nozzles

Tests were conducted with axial coal nozzles with a variety of spreader designs in both burner configurations. The spreaders consisted of two types: axial vane swirlers with vane angles ranging from 15 to 45°; and splitters which divided the primary air/coal into four streams and injected the fuel without swirl at angles from 30 to 60° (included angle).

Coal injection with reduced primary air flow (dense-phase transport) was also investigated. Primary air was reduced from approximately 1.9 to 0.2 kg air/kg coal. The diameter of the dense-phase coal nozzles was reduced in order to maintain the primary injection velocity at approximately 18 m/sec (60 ft/sec). Three injector types were used with dense-phase coal transport: a commercial spray nozzle; a conical spreader with a 30° included angle; and an axial vane swirler with a 30° vane angle.

Small Watertube Simulator (SWS) Furnace

The SWS facility is illustrated in Figure 2. The cylindrical test furnace has an inside diameter of 1.8 m (6 ft) and is 5.2 m (17 ft) in length. Burners are fired axially from one end of the cylinder, and the furnace is completely water jacketed with a partial refractory lining to control heat extraction. Gas temperature at the exit of the furnace is typically between 1000 and 1200°C (1800 and 2200°F). Nominal firing capacity is 2.9 MW (10×10^6 Btu/hr).

Fuels

A Utah high volatile bituminous coal was used for all coal tests. Analysis of the Utah coal is given in Table 1. Sorbent injection tests were conducted both with coal and with natural gas flames doped with SO_2. The sorbent used in these tests was commercially available limestone ($CaCO_3$) with a particle size distribution of between 3 and 45 m.

NO_x EMISSIONS

Figure 3 shows NO_x emissions obtained with various coal nozzles tested in the high velocity burner configuration. NO_x emissions are corrected to 0% stack O_2. Excess air was constant at approximately 20%, firing rate was 2.9 MW (10×10^6 Btu/hr), and combustion air preheat temperature was approximately 315°C (600°F). The data are presented as a function of gas temperature at the exit of the furnace. The variation in exit temperature is due primarily to the thermal inertia of the furnace cooling system and due to ash deposition in the furnace, which changes the extent of furnace heat extraction. The lines shown on Figure 3 and the following figures represent the "best fit" through data points obtained under similar burner operating conditions for each burner/nozzle combination. It can be seen that NO_x emissions generally increase with increasing furnace exit temperature for similar burner conditions, and that the dependence on temperature is unique to the specific nozzle/burner combination.

NO_x emissions as high as 925 ppm and as low as 350 ppm could be achieved through variation of coal nozzle design and burner adjustments. Most of the NO_x emissions data range between 500 and 750 ppm which is within the range encountered in the field for pre-NSPS boilers. It was difficult to reduce NO_x emissions below 450 ppm while maintaining satisfactory flame stability. High NO_x flames were generally characterized by low length-to-diameter ratios and by flame standoff between 0.1 and 0.6 burner exit diameters. The shaded area represents the range of emissions achieved with a 15° axial swirl vane nozzle by variations in burner adjustments, including adjustments to coal nozzle setback, coal spreader setback, secondary air distribution, and swirl distribution between the secondary air channels. These data show that NO_x can vary by as much as a factor of three depending only on burner adjustments. Data are also shown in Figure 3 for a splitter type nozzle which produced emissions in the range of 600-700 ppm. In this minimum flexibility burner configuration there did not appear to be a distinct advantage of utilizing the splitter type nozzle. It should be noted that, for all data presented in this paper, CO emissions were below 60 ppm and flames were stable.

Figure 4 shows the effect of adding a conical baffle to the inner secondary air sleeve of the high velocity burner (as shown in Figure 1) in order to divert some of the combustion air away from the main body of the flame, thereby reducing the local stoichiometric ratio in the initial regions of the flame. Adding the baffle did not appear to reduce NO_x emissions substantially for the splitter type nozzle. However, with the 15° axial vane swirler, NO_x emissions were reduced to between 225 and 500 ppm by adding the baffle. The baffle enhanced stability of the flames, and most of those conditions which produced low-NO_x emissions were associated with flames established well within the burner quarl. Comparison of these results with those shown in Figure 3 indicates that the air baffle substantially reduced the level of NO_x emissions from the high velocity burner configurations and dramatically increased the range of burner adjustment for which NO_x was below 400 ppm. The same range of conditions without the baffle typically resulted in NO_x between 700 and 900 ppm.

Figure 5 shows NO_x for several nozzles tested in the low velocity burner configuration. The shaded areas represent the range of NO_x emissions achieved with each nozzle design by variation of burner adjustments. The effect of increasing the burner throat diameter was most pronounced for one of the splitter coal nozzles (30° included angle) and for the 15° axial vane swirler. For equivalent burner and furnace conditions, NO_x reduction achieved with the low velocity burner was 51 percent for the splitter nozzle and 46 percent for the 15° axial vane swirler compared to results obtained in the high velocity burner.

NO_x formation in practical flames is determined to a large extent by mixing processes in the flame and heat transfer characteristics of the furnace. Flame shape is important because it reflects the mixing characteristics of the burner. Figure 6a shows a preliminary attempt at correlating NO_x emissions data with the observed flame dimensions for various coal nozzles in the low velocity burner. The flame dimensions are represented in Figure 6a by the observed flame length-to-diameter ratio (L/D). The shaded area on the figure represents the overall data trend for axial swirl vane nozzles.

There is a general trend for decreasing NO_x emissions with increasing flame length-to-diameter ratio, although there is noticeable scatter especially for low L/D (short flames). Data appear to fall above the shaded area when the flames are detached from the burner and fall slightly below the shaded area when the flame is sharply divided (e.g., with coal splitter nozzles).

Previous work by Payne, et al. (4) showed that NO_x emissions from oil flames produced by many different burners fired in different furnaces could be correlated by a factor which takes into account flame shape, furnace heat extraction, and entrainment characteristics of the flame. Since the bulk entrainment characteristics (defined by the Thring-Newby parameter) are constant for constant burner velocity and diameter, a similar correlation was checked for the low velocity burner configuration which accounts only for flame residence time (in terms of firing rate and flame volume) and furnace heat extraction. These parameters are expressed as $(Q/V_f) \times (1/H_e)$ where Q is the gross heat input in megawatts, V_f is the observed flame volume, and H_e is the heat extracted in the furnace in megawatts. As shown in Figure 6b the correlation appears to work well for a single coal nozzle, but yields different NO_x values for different nozzles. This indicates a need for another parameter which takes into account differences in near-burner mixing as a result of coal nozzle design. The figure does seem to suggest that, for equivalent flame and heat extraction conditions (i.e., at a given value for the abcissa), NO_x emissions are lower for the two splitter nozzles than for the axial vane swirler nozzle, and are lowest when dense-phase coal transport is utilized. Since the coal injectors are located axially in the center of the burner, the reduction in coal nozzle diameter associated with dense-phase coal transport (to maintain primary injection velocity) results in increased area available for secondary air flow. As a result the baseline secondary air velocity of 58 m/sec (190 ft/sec) was reduced to 44 m/sec (145 ft/sec) when dense-phase coal nozzles were used in the high velocity burner. Similarly, secondary air velocity was reduced from 24 m/sec (80 ft/sec) to 21 m/sec (71 ft/sec) when dense-phase coal nozzles were used in the low velocity burner. The reduction in NO_x achieved with dense-phase coal transport probably results from changes in mixing and flame characteristics brought about by the combined effect of reduced secondary air velocity and altered coal/air distribution.

SO_2 EMISSIONS

The injection of dry calcium-based sorbents such as limestone and dolomite into boiler furnaces offers a potentially less expensive means of reducing SO_2 emissions compared to post-boiler scrubbing. The practical limitations to achieving high SO_2 removal rates appear to be related to sorbent reactivity and residence time within the temperature range for which sulfation of the sorbent is possible. Favorable temperatures are usually encountered downstream of the burner zone in the upper furnace and superheater area of most U.S. boilers. Sorbent dispersion into the combustion products is easiest to achieve if the sorbent is injected through the burner itself; however, sorbent reactivity is sharply reduced when exposed to flame temperatures and coal mineral matter. Therefore, injection of the sorbent away from the burner has been suggested, either through ports near the burner throat or in the upper furnace, downstream from the burners.

Figure 7 shows SO_2 removal versus calcium-to-sulfur molar ratio (Ca/S) for various sorbent injection locations near the high velocity burner. The data shown in Figure 7 were obtained using natural gas fuel doped with pure SO_2. The coal spreader support pipe located on the axis of the coal nozzle (see Figure 1) was replaced with a natural gas injector. As shown in Figure 7, SO_2 removal is approximately the same regardless of sorbent injection location, which suggests that sorbent reactivity is equally limited for all near-burner injection locations. This indicates that it could be difficult to meet SO_2 capture objectives (50 percent SO_2 removal at Ca/S = 2.0) if the sorbent is injected near the burner.

Based on these results and results of other related EPA research programs, recent efforts under this program have concentrated on topics related to sorbent injection in the upper regions of a boiler furnace remote from the burner zone. In these upper regions, injection will typically be by means of jets, where some carrier medium (air or flue gas) will be required to ensure adequate penetration and dispersion of the sorbent. A particular emphasis has therefore been placed on the investigation of sorbent injection techniques, and whether available jet parameters offer any secondary means influencing the reactivity of sorbent materials. Interest has centered particularly on heating rate, and the potential use of double concentric jets to provide thermal shielding, either for conventional sorbents or for high reactivity materials (5,6) which may be very temperature sensitive.

The simplest injection scheme involves a single jet of sorbent material dispersed in carrier air. Figure 8a shows SO_2 removal for $CaCO_3$ injection using a single small-diameter (2.54 cm) sorbent jet injector along the axis of the SWS furnace. An array of small gas-fired burners was arranged around the sorbent jet to produce simulated combustion products at 1200°C (2200°F) flowing parallel to the sorbent jet. Natural gas doped with pure SO_2 was fired through these small gas burners, and the furnace walls were completely insulated to minimize heat extraction. Furnace gas temperature (background gas temperature) was approximately constant (within 15 percent) throughout the furnace. The velocity of the sorbent jet was varied by changing the transport air flow rate. SO_2 removal was similar for injection velocity of 30 and 15 m/sec (100 and 50 ft/sec) but was much lower for low injection velocity of 7.6 m/sec (25 ft/sec). Since the peak temperature experienced by the sorbent jet is believed to be approximately the same for all three injection velocities, it is believed that the heating rate in the initial regions of the jet may affect the development of surface area as the raw sorbent undergoes calcination to CaO. This implies that some degree of control over sorbent reactivity may be achieved by controlling injection parameters. However in this experiment, complete mixing of the sorbent and combustion products does not occur until they enter the exhaust duct, and slight differences in dispersion may account for the effect of sorbent velocity on capture. Further experiments are planned to evaluate this effect.

Figure 8b shows the effect of gas temperature near the point of sorbent injection (background gas temperature) for the 30 m/sec (100 ft/sec) sorbent jet. SO_2 removal decreases sharply as gas temperature is increased from 1200°C (2200°F) to 1540°C (2800°F). This suggests that the reactivity of the sorbent decreases as the background gas temperature increases. Thus, it is evident that in practical systems high sorbent temperatures must be avoided in order to prevent deactivation of the sorbent.

Sorbent injection through single small jets is the simplest way to introduce sorbent into the upper furnace of the boiler and may result in high sorbent surface areas if high peak temperatures can be avoided since rapid heating rates are easily achieved; however, it is difficult to achieve adequate mixing between the sorbent and furnace gases since jet penetration is limited with small single jets. Combining the single sorbent jet with a larger annular air jet provides a means for increasing total jet momentum, thereby increasing jet penetration to achieve adequate sorbent dispersion. A coaxial air/sorbent jet can also be designed to screen the sorbent from high temperature gases as well as control sorbent heating rate. This would allow significantly greater control over the ultimate reactivity of the sorbent. Figure 9 illustrates the effect of jet parameters on SO_2 removal with coaxial air/sorbent jets injected into 1425°C (2600°F) combustion products. Comparing these results with Figure 8b at 1425°C indicates that SO_2 removal at Ca/S ratio of 2 has been increased from 22 percent for the single jet to 29-35 percent with the coaxial jets. The results shown in Figure 9 indicate that a 20 percent relative variation in SO_2 removal can be achieved by varying velocity and diameter of the annular air jet. Although the absolute level of capture is low for $CaCO_3$ because the ultimate surface area is low, the relative enhancement of SO_2 removal achieved using the annular jet may be very significant for other sorbents which are more reactive. Experimental work is currently under way to investigate the impact of jet parameters on SO_2 removal efficiency with other sorbents and to further develop the relationship between sorbent injection parameters and SO_2 removal.

DISCUSSION

These results suggest that NO_x reduction on the order of 50 percent may be possible through modifications to the coal nozzle and/or secondary air distribution without modifying the burner throat, especially where uncontrolled NO_x emissions are high initially. For instance, it may be possible to reduce NO_x emissions from 500-750 ppm to 225-500 ppm by adding a baffle to the secondary air passage on a typical pre-NSPS burner. The use of dense-phase coal transport and secondary air baffles appears to be particularly effective with "minimum flexibility" high velocity burner configurations. The coal injector used with dense-phase coal transport can be smaller in diameter which decreases secondary air velocity significantly. Since dense-phase transport also tends to concentrate the coal near the axis of the flame, stabilizing the flame within the burner quarl results in low-NO_x emissions without excessively long or poorly defined flames. However, since most coal mills are designed to operate with a fixed primary air flow, dense-phase coal transport may not be feasible without extensive modifications to existing coal delivery systems. Secondary air baffles used with high velocity burner configurations tend to promote stability of the ignition front within the burner quarl as well as divide the air flow for delayed mixing and are, therefore, effective in reducing NO_x emissions, particularly for detached flames.

These data tend to support the conclusion that, for high secondary air velocity, coal nozzles which concentrate the coal in a narrow region on the flame axis will tend to produce low-NO_x emissions if the flame is stabilized within the burner quarl. Coal nozzles which divide and disperse the coal stream to wide angles result in relatively faster mixing and therefore do not achieve significant NO_x reductions. For burners with low secondary air velocity, flames generally tend to be bigger than for burners with high secondary air velocity, and burner adjustments have a more significant impact on NO_x. Coal nozzles in low velocity burners which divide the coal to produce smaller separate flames produce lower NO_x emissions if the separation between the smaller flames is not clearly defined; however, if the injection angle is too wide or the flame is detached, coal and air mix more rapidly and smaller NO_x reductions are achieved.

Although sorbent injection near the burners is desirable to achieve mixing of the sorbent with the combustion products, thermal deactivation of the sorbent appears to be unavoidable and injection away from the high temperature burner region is more attractive, particularly for very reactive (high surface area) sorbents. Coaxial air/sorbent jets can be used in upper furnace sorbent injection to control sorbent dispersion by proper jet design. Coaxial jets also appear to offer a means for injecting sorbent into the upper furnace which allows additional control over those parameters which affect sorbent reactivity. The annular air jet can be particularly effective in reducing the extent of thermal sorbent deactivation when injection into high temperature regions of the furnace is necessary.

These results have also indicated that the heating rate of the sorbent in the initial region of the jet may influence the development of surface area during calcination. Since heating rate is affected by the entrainment characteristics of the jet, it may be possible to optimize jet design to achieve maximum sorbent reactivity. Further information is required to define the exact nature of the relationships between jet design and the overall SO_2 removal process for sorbents which exhibit differing characteristics.

ACKNOWLEDGEMENTS

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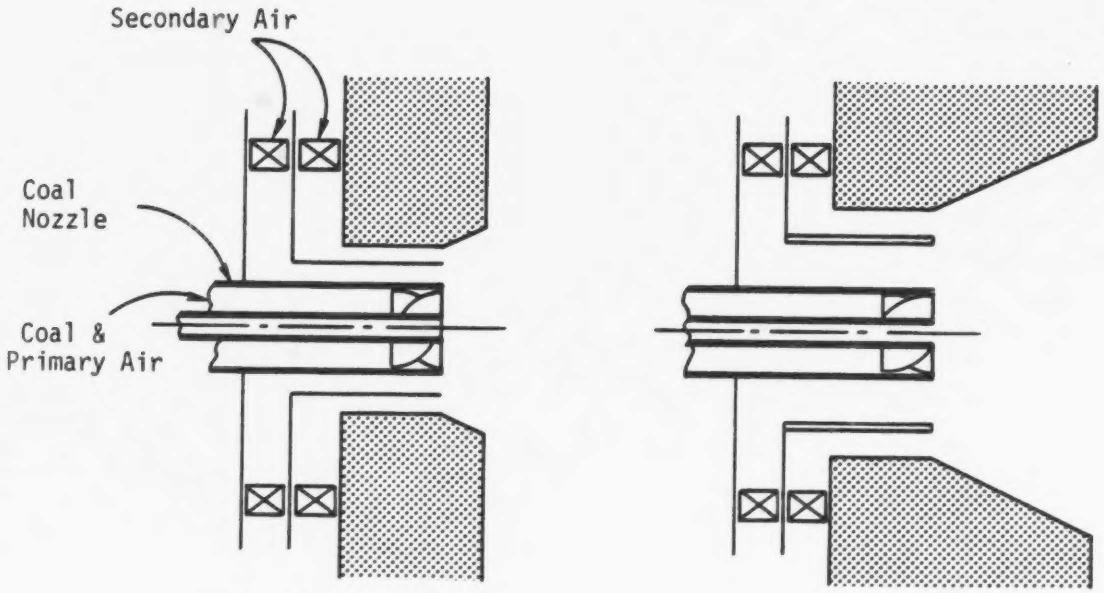
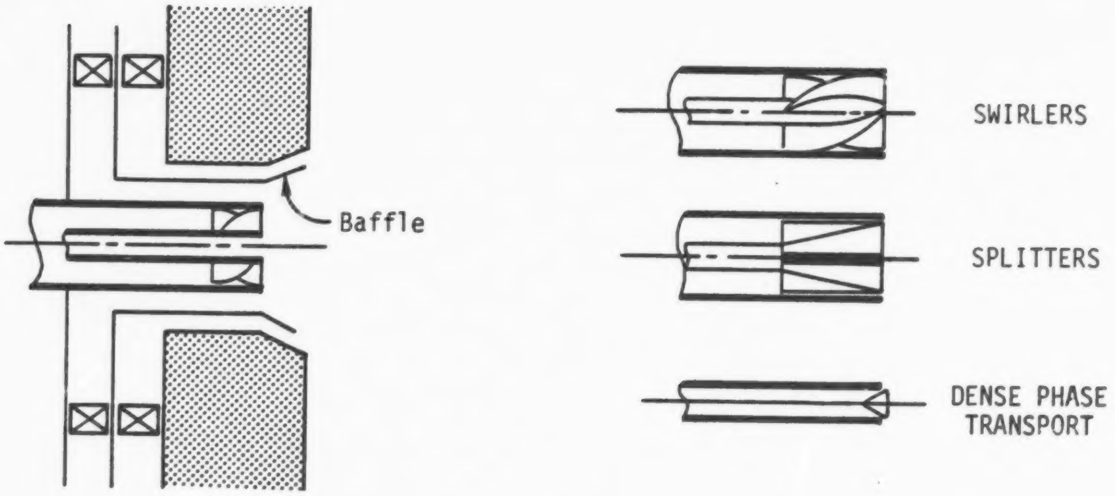

Secondary Air
Coal Nozzle
Coal & Primary Air

HIGH VELOCITY BURNER
58 m/s (190 ft/sec)

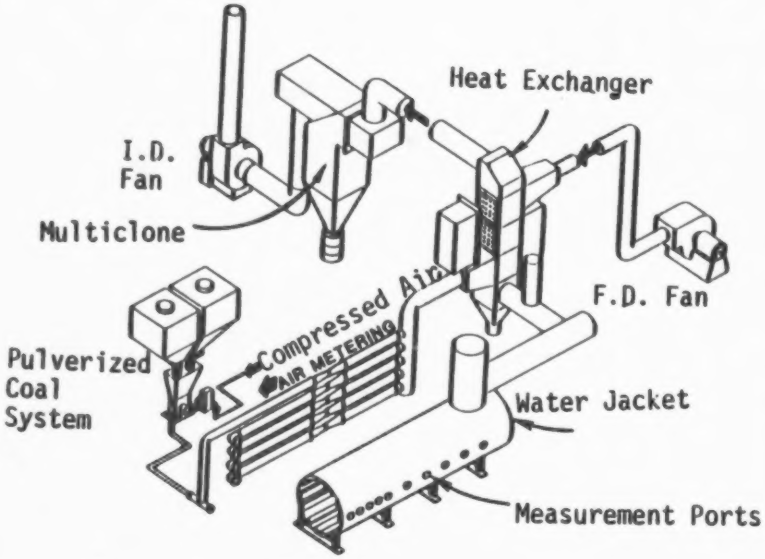
LOW VELOCITY BURNER
24 m/s (80 ft/sec)


Baffle
SWIRLERS
SPLITTERS
DENSE PHASE TRANSPORT

SECONDARY AIR BAFFLES

COAL NOZZLES

Figure 1. Experimental burners.



Heat Exchanger
I.D.
Fan
Multiclone
Compressed Air
AIR METERING
F.D. Fan
Pulverized
Coal
System
Water Jacket
Measurement Ports

Figure 2. Small watertube simulator facility.

CHARACTERISTICS	
Shape	Cylinder
Diameter	6 Ft (1.8 m)
Length	17 Ft (5.2 m)
Refractory Insulation	50%
Volumetric Heat Release	20,000 Btu/Hr-Ft^3 (0.21 MW$_t$/m^3)
Firing Rate	10 x 10^6 Btu/Hr (2.9 MW$_t$)
Heat Release Per Cooled Surface	60,000 Btu/Hr-Ft^2 (0.19 MW$_t$/m^2)
T Exit (Typical)	1800°F - 2200°F (980°C - 1200°C)

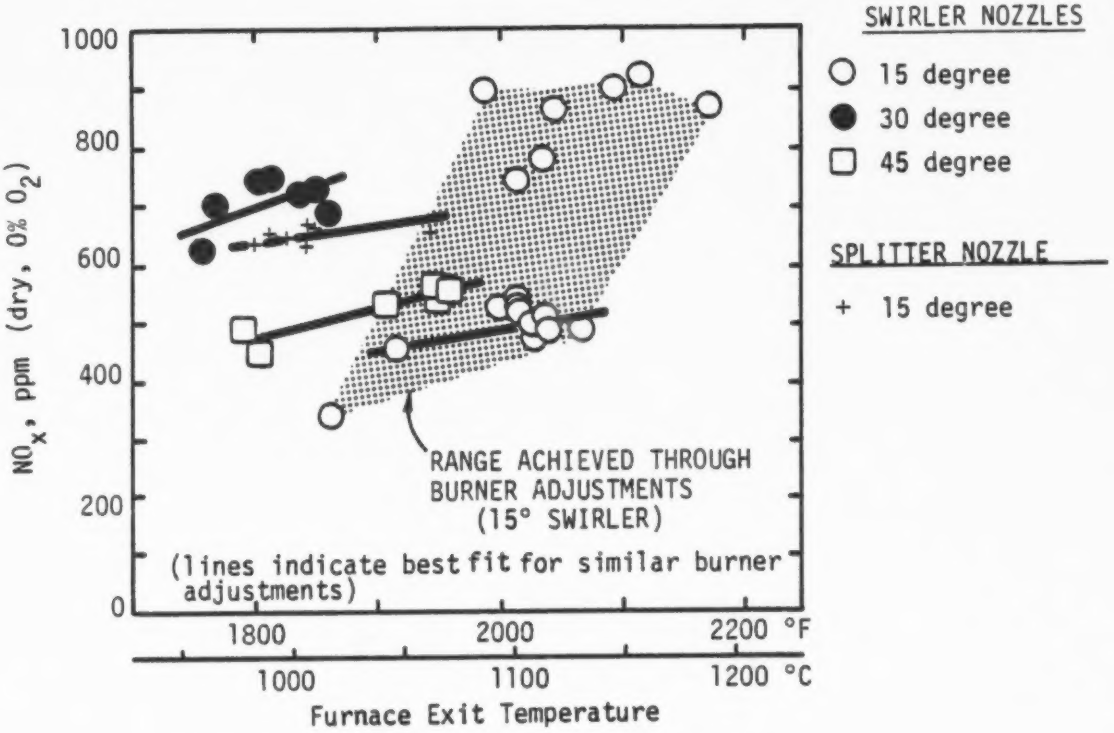


Figure 3. NO$_x$ emissions achieved with high velocity burner.

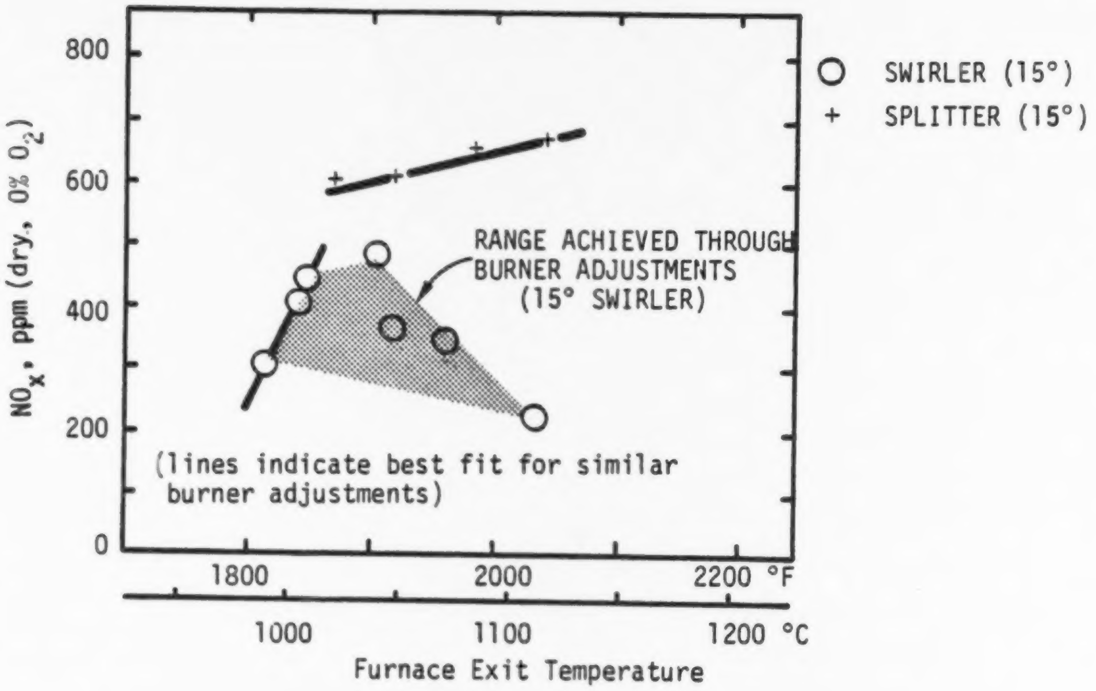


Figure 4. NO_x emissions with secondary air baffle added to high velocity burner.

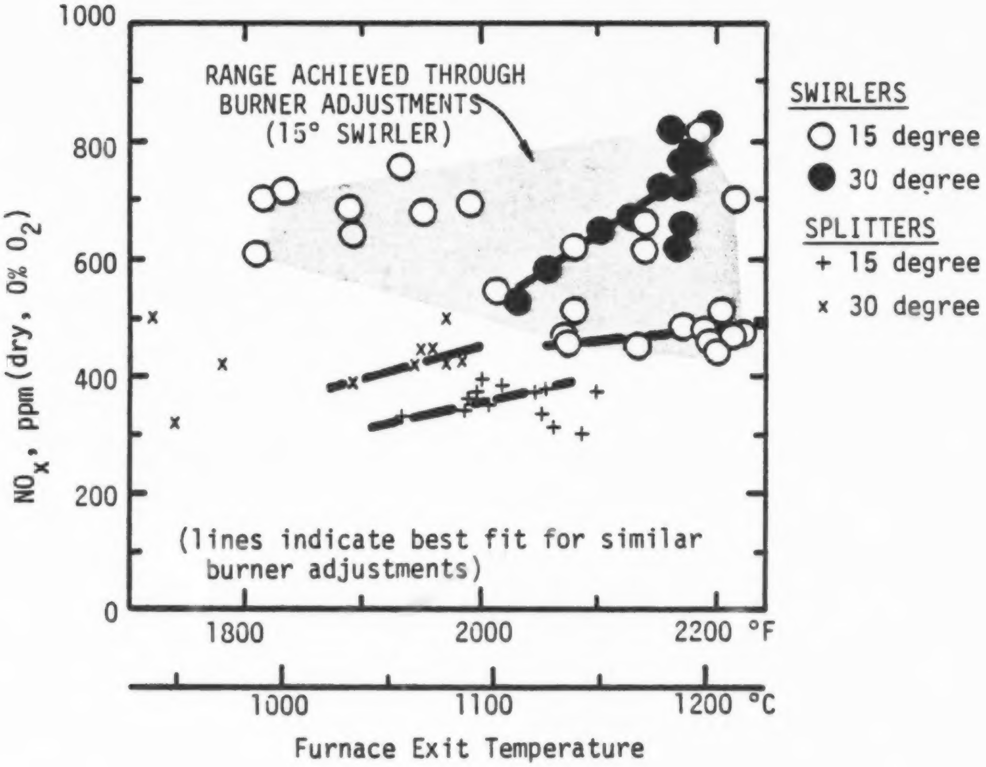
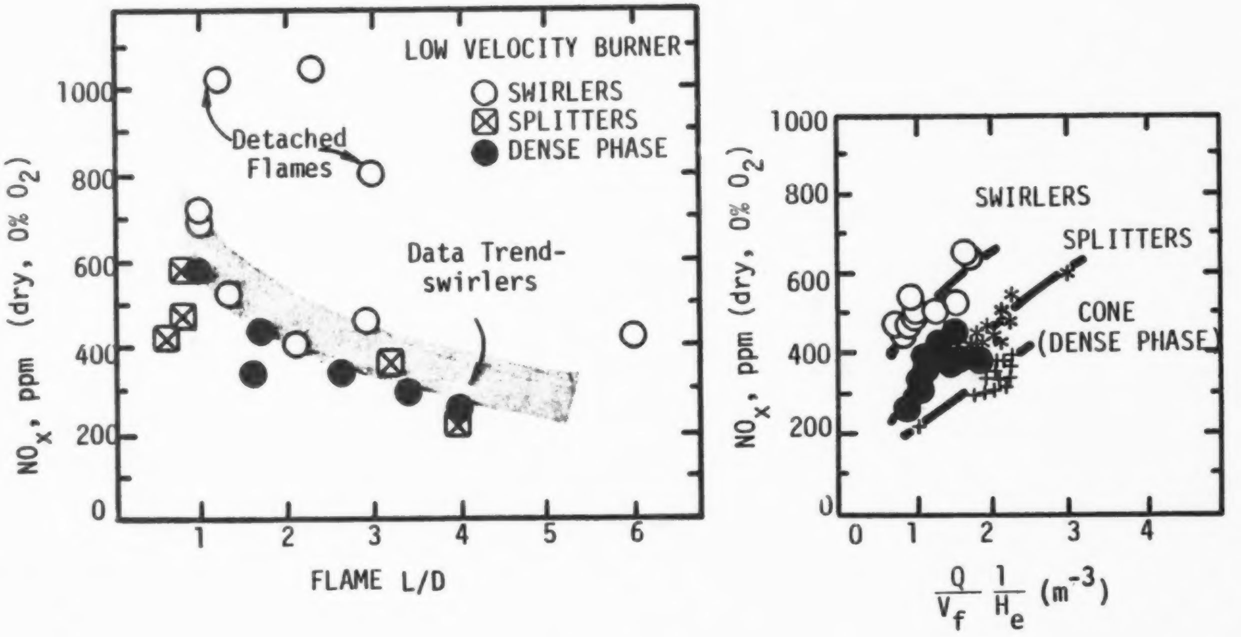


Figure 5. NO$_x$ emissions with low velocity burner.



(a) (b)

Figure 6. Relationship between NO_x and (a) flame shape, and (b) flame/furnace parameters.

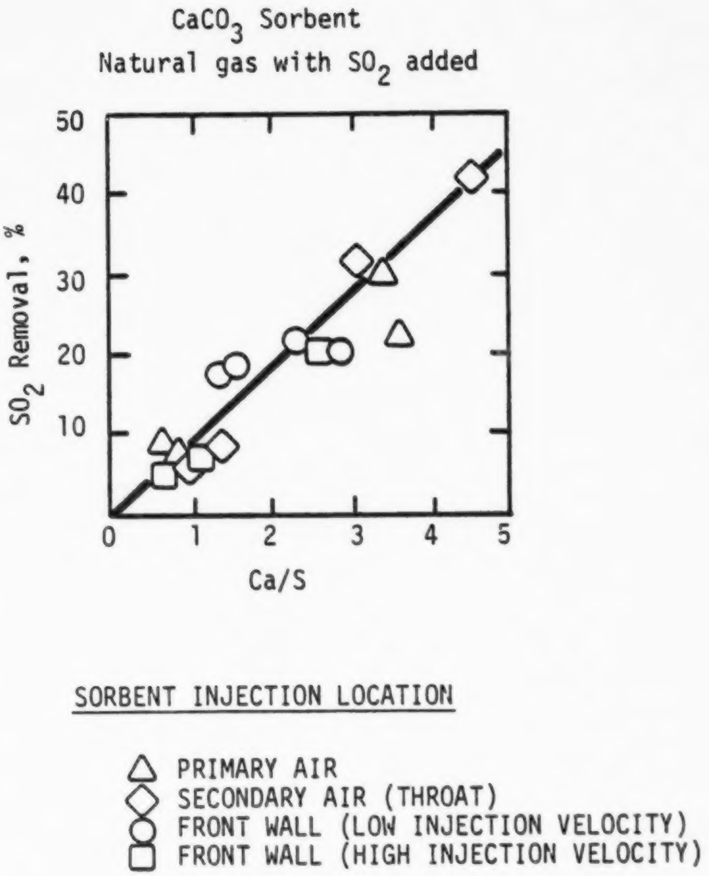
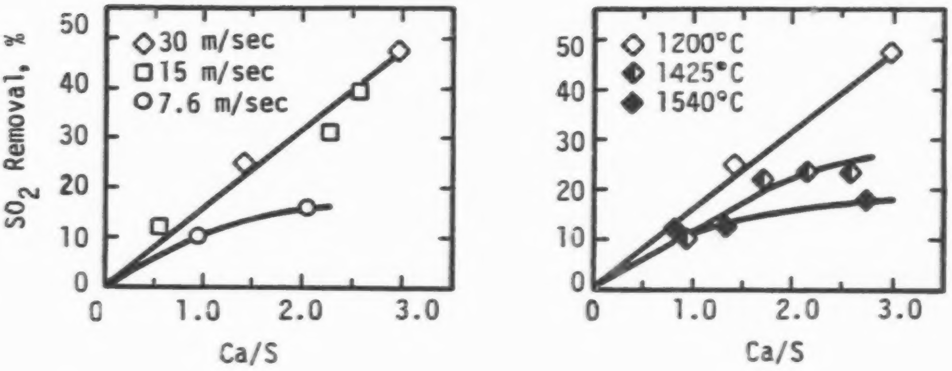


Figure 7. Near-burner sorbent injection--effect of injection location (2.9 MW, high velocity burner).



(a)

(b)

Figure 8. SO_2 capture in single sorbent jets for (a) 1200°C background gas temperature and (b) 30 m/sec sorbent injection velocity.

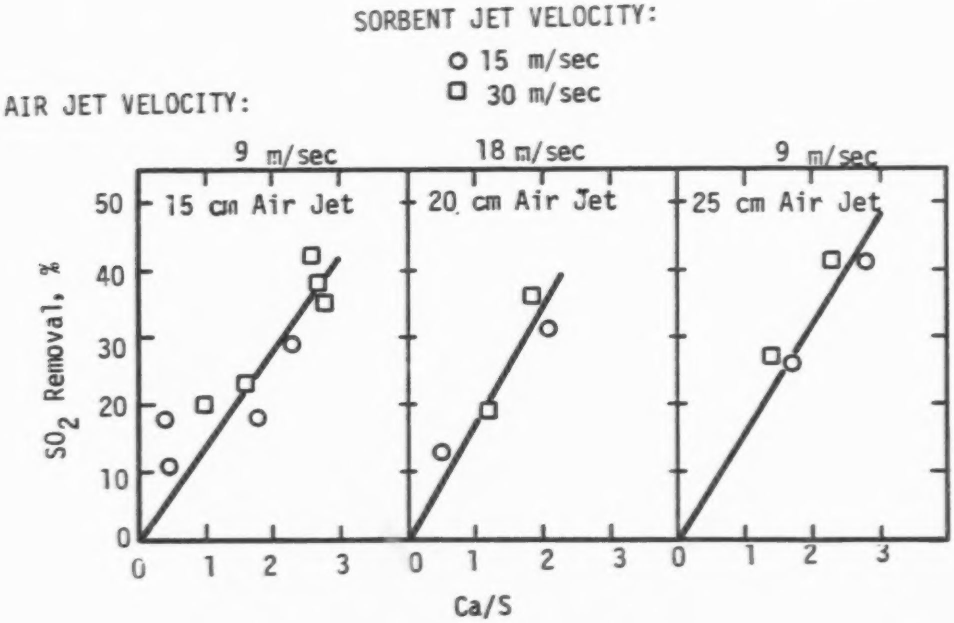


Figure 9. Effect of jet velocity and diameter on SO_2 capture for sorbent injection in coaxial air/sorbent jets (background = 1425°C).

TABLE 1. ANALYSIS OF UTAH COAL

	As Received	Dry Basis
Ultimate Analysis:		
C (%)	67.42	69.61
H (%)	5.02	5.18
N (%)	1.38	1.42
S (%)	0.67	0.69
O (%)	12.71	13.12
Moisture (%)	3.14	---
Ash (%)	9.67	9.98
Gross Heating Value (kJ/g)	---	30.39
Gross Heating Value (Btu/lb)	---	13,066

SESSION V: POST-FURNACE SO_2 REMOVAL

Chairman, Dan Giovanni, Electric Power Technologies, Inc.

CHARACTERIZATION OF ALTERNATE SODIUM SORBENTS FOR FABRIC FILTER SO_2 CAPTURE

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University Park Station
Denver, Colorado 80210

ABSTRACT

Injection of dry-sodium powders into the inlet plenum of fabric filters (baghouses) has been demonstrated to be an effective flue gas desulfurization (FGD) technique. On a full-scale utility boiler, injected sodium products have been shown to meet New Source Performance Standards (NSPS) of 70% removal for low-sulfur coal applications. Higher levels of SO_2 removal have also been demonstrated with the injection of greater quantities of sodium reagent. The amount of reagent required is shown to be sensitive to the reagent particle diameter. Results are given for commercially available sodiumbicarbonate, trona, and light soda ash (sodium carbonate). Supply of sodium reagents is becoming increasingly more abundant as several chemical commodity suppliers expend both research and venture capital dollars to enter the potential utility market. To date, sodium bicarbonate reagents have been shown to provide better sodium utilization than sodium carbonate and trona.

INTRODUCTION

Background

The process of combining SO_2 and particulate control using dry-sodium reagents is gaining increased utility interest. This paper reviews and updates events relevant to the use of dry-sodium-based injection into the inlet of a fabric filter.

The Electric Power Research Institute (EPRI) is interested in evaluating the advantages and disadvantages of dry-sodium injection because the technology has the potential to greatly simplify hardware requirements, and to significantly reduce the capital requirements for both new and retrofit SO_2 control applications. Evaluating the importance of simplicity is qualitative, but may be weighted heavily by utilities concerned about operation and maintenance of emission control equipment.

EPRI began studying dry-sodium injection in 1977. To date, it has published feasibility study results (1), bench-scale investigation results (2), and full-scale demonstration results obtained in testing at the 22 MW Cameo station of the Public Service Co. of Colorado (3). An economic evaluation of dry-sodium injection is scheduled to be published soon. Work is now being conducted at EPRI's Arapahoe Test Facility in Denver to characterize and assess potential new dry-injection reagents for utility applications. Results from this pilot scale work and their implication to the full scale application are the subjects of this paper.

Figure 1 is a simplified flow schematic of a coal-fired power plant with dry-sodium injection for SO_2 control. Unit processes are much the same as those required for coal handling: transportation, storage, pulverization, and injection.

With dry-sodium injection, the sodium reagent is fed into the flue gas stream (nominally at a temperature of $300^{\circ}F$) ahead of a baghouse and downstream of the air heater. In the ductwork, the sodium bicarbonate in the reagent particles decomposes to sodium carbonate (Na_2CO_3) in a "popcorn" fashion, forming an open porous microstructure and exposing more particle surface area. The Na_2CO_3 reacts with the SO_2 in the flue gas and subsequently collects along with fly ash on the bags in the baghouse as part of the dustcake, further removing SO_2. Both the spent reagent and the filtered fly ash on the bags are then removed in the normal course of bag cleaning and collected for disposal. Typically, 70-80% of total SO_2 removal occurs in the baghouse, and the remaining 20-30% in the ductwork.

Dry-sodium injection offers a number of advantages over alternate SO_2 collection options. These include:

- Capital costs are significantly lower because of the comparative simplicity of the process.
- Only equipment already in common use at coal-fired power plants is required.
- No wet slurry or sludge is required.
- The systems are easily retrofitted to boilers equipped with baghouses.
- Power costs are low.
- Scaling and corrosion are minimal.
- Flue gas reheating is not necessary.

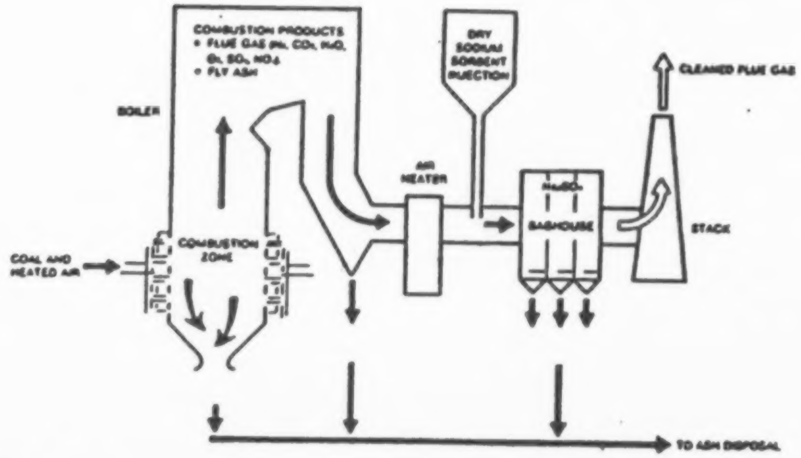
COMBUSTION PRODUCTS
• FLUE GAS (N2, CO2, H2O, O2, SO2, NOx)
• FLY ASH
BOILER
DRY SODIUM SORBENT INJECTION
CLEANED FLUE GAS
AIR HEATER
Na2SO4
BAGHOUSE
STACK
COMBUSTION ZONE
COAL AND HEATED AIR
TO ASH DISPOSAL

Figure 1. Schematic of a coal-fired power plant with dry-sodium injection for SO_2 control.

Reagent Availability

Sodium reagents that have received the most utility and supplier attention include nahcolite (naturally occurring sodium bicarbonate, $NaHCO_3$), trona (naturally occurring $NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$). Huge supplies of both nahcolite and trona are estimated to exist in the United States: over 30 billion tons of nahcolite, and in excess of 85 billion tons of trona.

Nahcolite is the preferred reagnet because of its high bicarbonate content and, in tests conducted to date, its high sodium utilization. Permits were filed in October 1984 to begin commercial solution mining of nahcolite in the Piceance Basin in Colorado. Trona is commercially available in large quantities. Both have been shown to easily achieve 70%-plus SO_2 removals.

Given the promise of dry-sodium injection for SO_2 control, several companies have recently expressed interest and/or begun offering processed reagents for use of utilities. A list of these companies is given below in Table 1. This list demonstrates the dramatic turnaround in available suppliers of reagent. Only a few years ago, no firm suppliers could be identified.

TABLE 1

SUPPLIES OF SODIUM - BASED REAGENTS - 1984

Allied Chemical Corporation
Cominco American
Church & Dwight Company, Inc
Industrial Resources, Inc
FMC Corporation
Kerr-McGee Chemical Corporation
Natrona Ind
Stauffer Chemical Company
Tenneco
Texas Gulf Chemicals Company

This potential for improved product availability has increased the level of utility interest in a more detailed analysis of dry-injection. Also, and significantly, these suppliers are developing improved processed reagents which have substantially lower fractions of inert material. This means less inert material to be transported and stored by the utility, thereby lowering overall reagent costs.

PILOT PLANT DESCRIPTION

The dry sodium injection pilot plant (Unit 3A) is located at the EPRI Arapahoe Emissions Test Facility (Denver, Colorado). Flue gas for the pilot plant is withdrawn at the rate of 1250 scfm from Public Service Company of Colorado boiler number 4 (100MW nominal load). In the pilot plant, injection of reagent materials is accomplished by continuously moving sorbent from a small hopper via a screw feeder into the suction port of an eductor (Figure 2). Approximately 5 cfm of carrier air transports the reagent materials into the duct at a point 6 ft upstream of the baghouse inlet. Flue gas velocity at the point of injection is approximately 60 fps. A scale continuously determines feeder system weight during testing. This parameter is recorded so that a loss of weight over time may be deteremined. Gas concentrations of SO_2 and O_2 are continuously monitored at both the system inlet and outlet. Near constant inlet SO_2 concentrations are maintained by an SO_2 dosing system. NOx levels are determined by using a single NOx analyzer continuously switched between the system inlet and outlet for discrete sampling periods. The pilot plant is in full time operation using a three hour reverse gas fabric filter cleaning cycle. Numerous controls and test parameters, including gas flow, temperature, and baghouse pressure drop are continuously monitored.

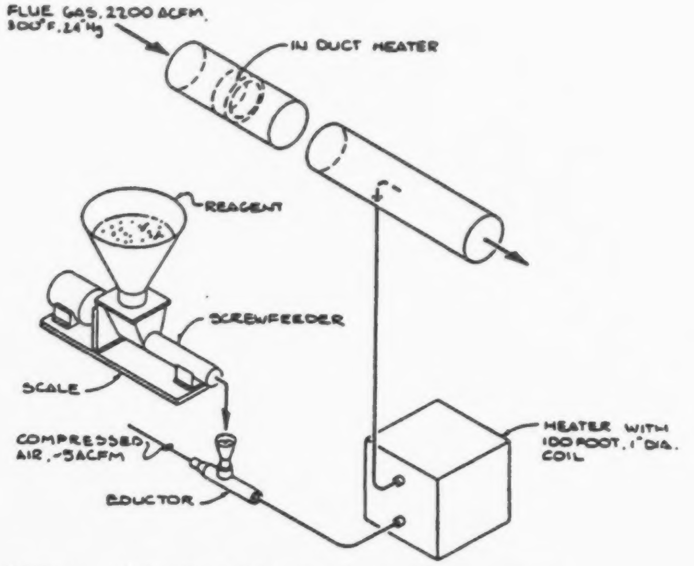

Figure 2. Illustration of Unit 3A pilot plant dry injection feed system at Arapahoe.

DISCUSSION OF RESULTS

Sodium Bicarbonate

The technical aspects of dry-sodium injection have been studied by several researchers over the past few years. The most important is the utilization of sodium in the reagent. Figure 3 illustrates SO_2 removal versus NSR (normalized stoichimetric ration) for low-sulfur (0.5%), western coal obtained with nahcolite, at the bench-scale, and at the full scale Cameo demonstration. SO_2 removal is shown to improve substantially from the bench-scale to the full-scale. A major reason for this improved utilization is now believed to be associated with reagent particle size distribution. The reagent at Cameo was pulverized much finer than those for the bench-scale research. Results published by other researchers are similar to those reported on the bench-scale; the results from the Cameo demonstration reported the highest sodium utilization of any previous work.

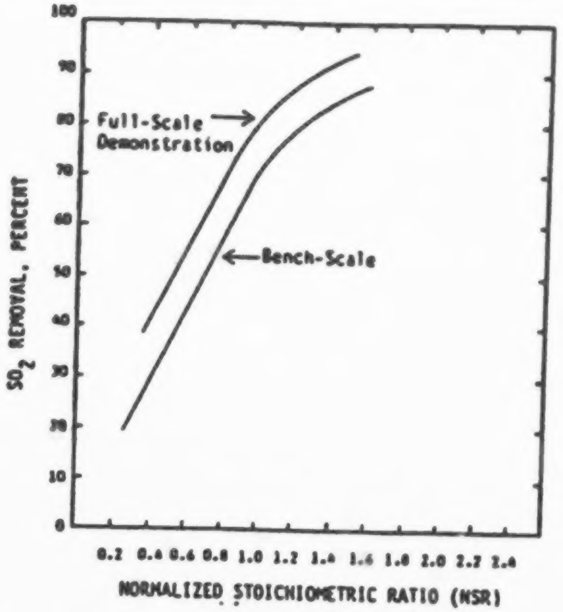

Figure 3. SO_2 removal vs. NSR for nahcolite illustrating improvement in results reported from the bench-scale to the full-scale. Tests conducted with low-sulfur (0.5%), western coal.

EPRI is currently conducting pilot-scale research to evaluate the effectiveness of the numerous new reagents now being offered. This work is being conducted by KVB, Inc at Arapahoe.

Figure 4 illustrates SO_2 removal versus NSR (normalized soichiometric ratio) when injecting sodium bicarbonate of five (5) distinctly differing characteristic particle sizes. These results have many implications to the application of dry injection technology.

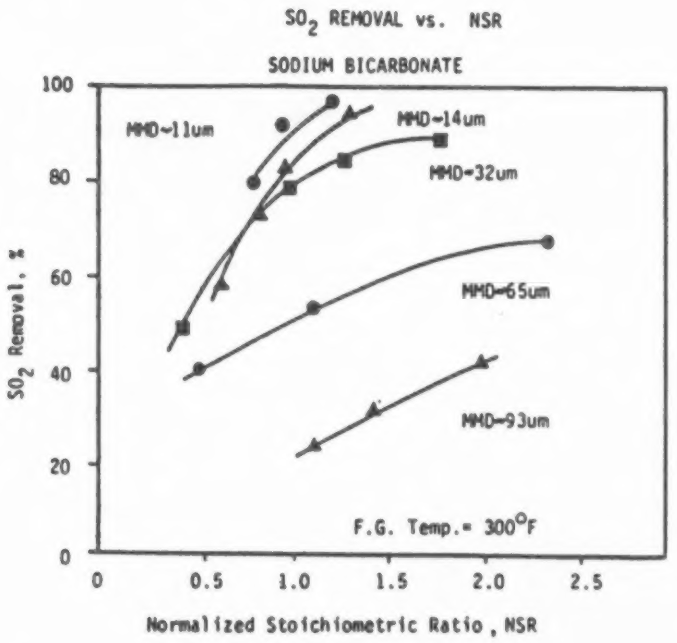

Figure 4. SO_2 removal vs. NSR for sodium bicarbonate illustrating the dependence of SO_2 to the MMD (mass mean diameter) injected into the flue gas duct.

First, SO_2 removal is shown to significantly improve with decreasing reagent particle size and SO_2 removal greater than 90% is illustrated for the finest particle sizes. Note, however, that a significant amount of energy may be required to pulverize reagents to a size necessary to optimize sodium utilization (SO_2 removal divided by NSR). Fortunately, these sodium bicarbonate reagents should be easily pulverized in comparison to the conventionally mined ores of trona and nahcolite.

Second, it should be noted that the sodium bicarbonate for these tests was provided by three reagent suppliers each using different methods to process their reagent. Even using bicarbonates mined and processed by different methods, the results were consistent--sodium utilization with bicarbonate injection is apparently a function of particle size, not manufacturing method. The sodium bicarbonate reagents used to produce this data were provided by Church and Dwight, Kerr-McGee, and Industrial Resources, Inc.

Third, the advantage of smaller reagent size does not appear to be caused by the increasing specific surface area of the reagent (specific surface is inversely proportional to particle diameter) but more likely because of better reagent distribution throughout the baghouse. Figure 5 is an illustration of the baghouse compartment of the Unit 3 pilot plant. It can be seen that the required path for a reagent particle to reach the bag thimble in the corners nearest the inlet is much more treacherous than to reach the bags directly opposite the inlet duct. This is even more dramatic for larger reagent particles. To optimize SO_2 removal, particles must be small enough to follow the gas stream and distribute evenly across the tubesheet to each bag inlet. The result of maldistribution is that some bags become enriched with reagent and some are starved. This appears to be the mechanism that increasingly degrades SO_2 removal as reagent particle diameter increases (as illustrated in Figure 4).

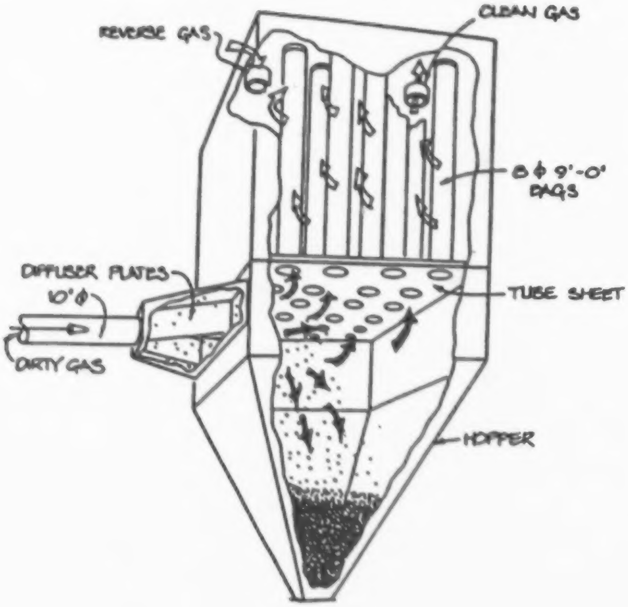

Figure 5. Illustration of the baghouse compartment of the Unit 3A pilot plant.

These findings are important when considering injection design criteria, reagent pulverization requirements and techniques, and possibly baghouse inlet transition and hopper designs. For example, the requirements on a pulverizer for dry-injection might be slightly more demanding (i.e., finer particles required) when the boiler load is reduced and the gas flows are lessened. The carrying velocity into a baghouse compartment hopper needs to be sufficient to keep a reagent particle from falling out; and the reagent distribution needs to remain somewhat uniform across the tubesheet. This underlines the importance of a good aerodynamic modeling effort relating to the injection system and baghouse designs, especially at lower boiler steam loads where flue gas flow rates are substantially lower than design specifications.

Flue gas temperature has been demonstrated to affect reagent utilization of sodium bicarbonate as temperatures range between 260°F and 340°F. This is shown in Figure 6 where SO_2 removal is plotted versus NSR for a reagent injected at 300°F and 330°F (Figure 6a) and for another reagent injected at 260°F and 300°F (Figure 6b). These temperatures generally span normal operating temperatures for utility baghouses. These curves also show that reagent particle specification can be matched with baghouse inlet temperature specifications as a trade-off in system design considerations.

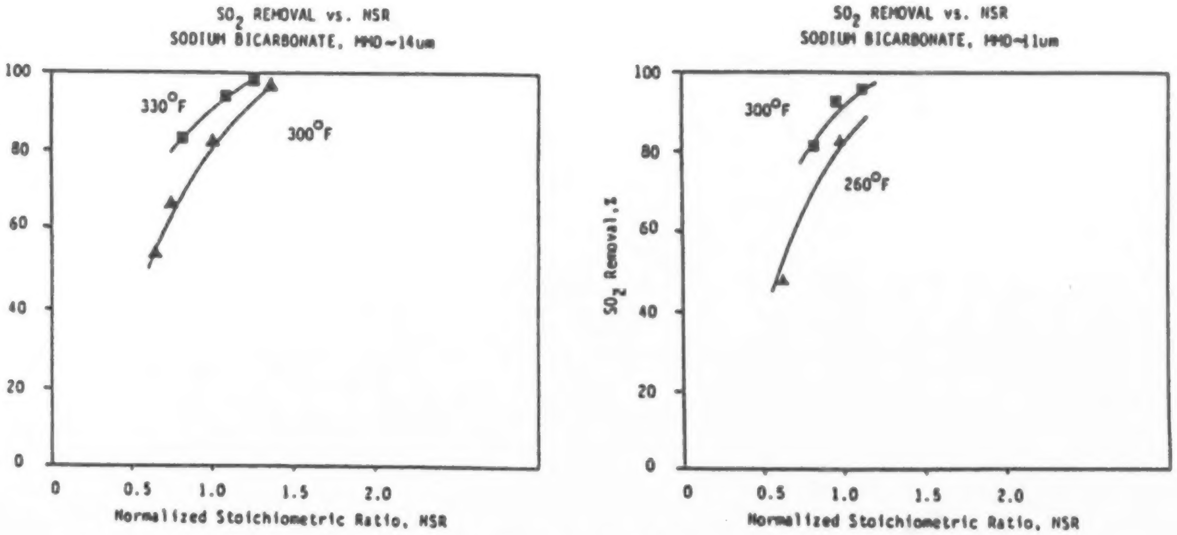

Figure 6 (a & b). SO_2 removal vs. NSR for two sodium bicarbonate reagents illustrating the dependence of SO_2 removal to flue gas temperature.

Trona

Trona was acquired for this project from Wyoming by TenneCo and from California by Kerr-McGee. The materials were pulverized into size fractions and treated in the same manner as done previously with the bicarbonate reagents. Although characteristic size dimension measurements have not been completed, the reagents were provided in distinct size fractions allowing tests to be performed that generated the data shown in Figure 7. These results follow the same trend as previously shown. Note, however, the significant differences in sodium utilization between the bicarbonate (Figure 4) and trona (Figure 7) reagents. Again, utilization is calculated as SO_2 removal divided by NSR. Until more complete characteristic size information is available, the size fractions indicated will suffice as relative indicators of reagent size.

Figure 8 is a graphic of the affect that flue gas temperature has on SO_2 removal when injecting trona. Although a more complete series of tests are needed to identify a perferred operating temperature, it is important to note that increasing the flue gas temperature decreases the effective SO_2 removal of trona. This is directly opposite the trend shown for sodium bicarbonate.

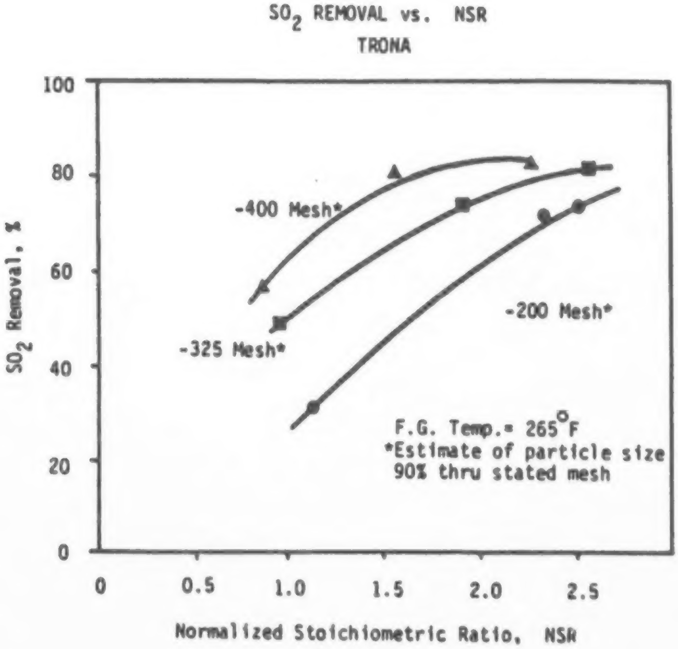

Figure 7. SO_2 removal vs. NSR for Trona illustrating the dependence of SO_2 removal to the MMD of the reagent.

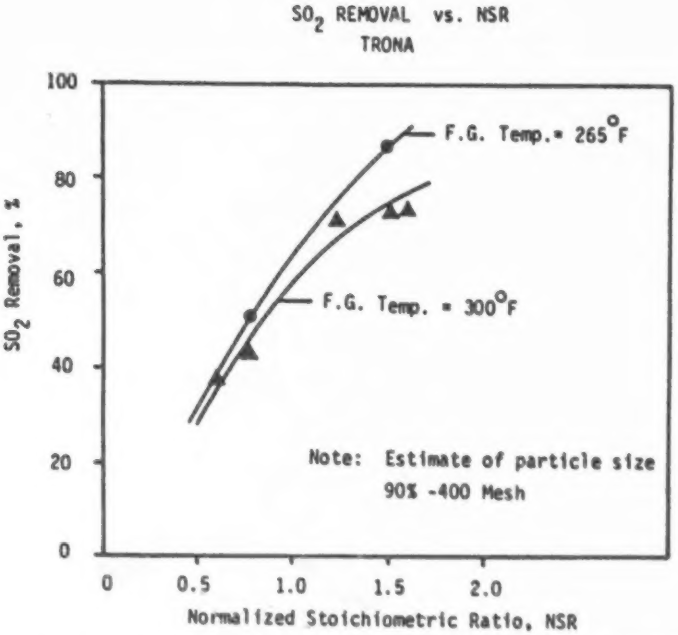

Figure 8. SO_2 removal vs. NSR for Trona illustrating the dependence of SO_2 on flue gas temperature.

Soda Ash

Previously reported results from tests that directly inject soda ash (sodium carbonate) into the flue gas demonstrate SO_2 removal below 20% for NSR values greater than two (NSR > 2)[3]. However, at Arapahoe, sodium carbonate injection has demonstrated substantially more SO_2 removal than previously reported. The results shown in Figure 9 were produced by injecting a "light ash" provided by Kerr-McGee. "Light ash" reagents produced by other suppliers are also scheduled to be tested. Shown in Figure 10 is the collage of results from the injection of sodium bicarbonate, sodium carbonate, and trona. The reagents were provided by a single supplier, pulverized to a similar particle size, and each injected at 300°F. It is of interest to observe that mathematical addition of SO_2 removal from a one-to-one molar mixture of sodium bicarbonate and sodium carbonate (as in the chemical formula for trona) produces an SO_2 removal nearly equal to that empirically obtained when injecting trona.

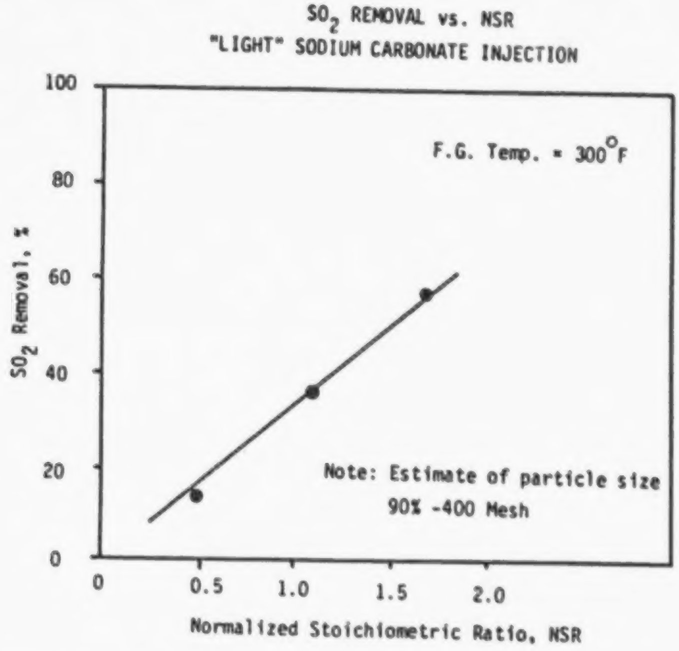

Figure 9. SO_2 removal vs. NSR for "light" sodium carbonate.

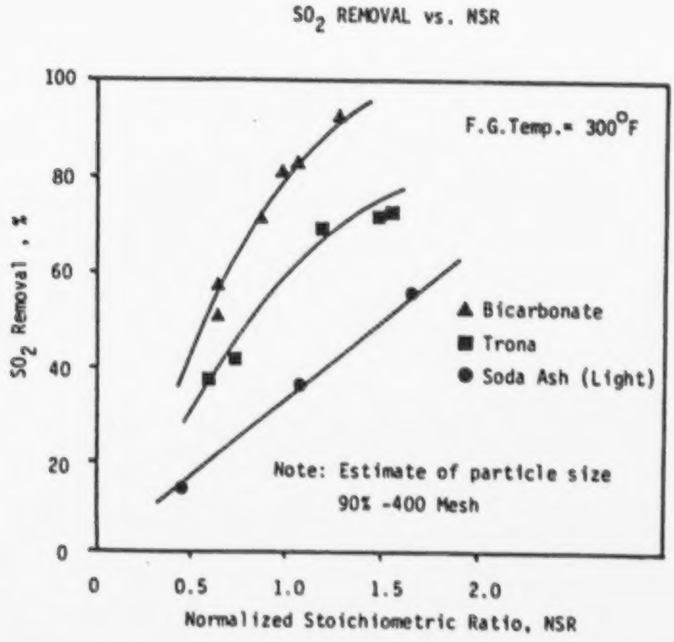

Figure 10. SO_2 removal vs. NSR for three reagents produced from a single feed stock by Kerr-McGee.

SUMMARY

The few and simple unit processes required to successfully operate a dry-injection system make the technology an attractive, economic alternate for SO_2 control on coal-fired power plants. The interest of several large, potential suppliers in entering the market is especially promising in terms of making available better performing and lower cost reagents. Dry-sodium injection systems designed to optimize reagent utilization will provide benefits in all areas of the technology, minimizing reagent and solids handling requirements, hopefully lowering levelized costs, and reducing the sodium levels in the fly ash waste product.

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3. L. J. Muzio, T. W. Sonnichsen, "Demonstration of SO_2 Removal on a 22 MW Coal-Fired Utility Boiler by Dry Injection of Nahcolite," CS-2894, Vol. 1, March, 1983; Vol. 2, June 1984, Electric Power Research Institute, Palo Alto, CA.

4. R. W. Scheck, D. J. Naulty, A.E.E. Gallagher, R. P. Grimm, D. A. McDowell, R. J. Keeth, J. E. Miranda, "Economic Evaluation of Dry Injection FGD Technology," RP-1682-1, Electric Power Research Institute, Palo Alto, CA.

DRY INJECTION SCRUBBING OF FLUE GASES BY THE SHU PROCESS

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ABSTRACT

The SHU dry sorbent injection process has been installed at the Ruhr recycling center refuse incinerator to remove stack gas SO_x, HCl, and HF. The incinerator produces 60,000 to 142,000 m^3/h of flue gas with typical or design concentrations of 70 to 275 ppm SO_x, 300 to 1,080 ppm HCl, and 20 ppm HF. Prior to gaseous pollutant cleanup, particulates are removed in an electrostatic precipitator, and the combustion gases are cooled to 200 to 220°C by heat exchangers. Dry scrubbing occurs in a contact section fed by calcium hydroxide and steam at a feed ratio of 0.5 kg steam/kg $Ca(OH)_2$. The feedrate is metered based on the pollutant level in the treated gas. The flue gas, $Ca(OH)_2$ and steam are swirled to enhance contact and absorption. Following absorption, spent sorbent is removed by a fabric filter. The unit entered service in 1982. Test results show SO_2 removal efficiencies of 55 to 85 percent, depending on inlet concentration, and HCl removal efficiency usually over 90 percent. Selected solids analyses showed approximately 37 percent calcium hydroxide consumption corresponding to a utilization ratio of 1:2.7.

INTRODUCTION

The SHU dry injection gas scrubbing process has been developed and applied by Saarberg-Hölter Umwelttechnik GmbH which was formed in 1974 as a joint property of the power plant operator Saarberg AG and the engineering firm Hölter GmbH, Gladbeck. Saarberg AG is an integrated energy firm operated by the Federal Republic of Germany and the Saarland. They are the second largest producer of hard coal in West Germany and their power plants account for 50 percent of electricity generated in the Saarland. Hölter GmbH, Gladbeck is an engineering and construction company supplying environmental control systems, coking plants, and foundries. The SHU process is marketed by four licensees or partners:

- S-H-L, Saarberg-Hölter Lurgi GmbH, Saarbrücken, West Germany
- Davy McKee Corporation, Lakeland, USA
- Simmering-Graz-Pauker AG, Austria

- BV Koninklijke Maatschappije "de Schelde", Netherlands
- Groupement with Lurgi S.A., France

Table 1 lists current and planned installations of SHU systems. This paper summarizes the application to the Ruhr recycling center (RZR) which is the first large-scale incineration installation of the dry scrubbing process. The process was previously tested in a pilot plant at the waste incineration center at Ebenhausen in Bavaria.

FACILITY

RZR produces electric power and district heating by burning approximately 100,000 tonnes/year of domestic and bulk refuse in a stoker-fired furnace. Incoming bulk refuse is shredded by two cylindrical cutters and stored in a bunker from which it is transferred by crane, together with domestic refuse, to the stoker-fired furnace. The refuse is extremely heterogeneous with wide fluctuations in heat content and composition. In the furnace, these fuel fluctuations produce variations in furnace temperature (held below 800°C), flue gas concentration, and particulate loading. Surplus heat in the stoker combustion gases is used in a heat recovery boiler to produce up to 57 tonnes/hour of steam (1). Solid particles are removed from the boiler stack gas in an electrostatic precipitator and the gas is then passed to the dry scrubbing process.

The dry scrubing system is designed in two sections, each with a cooler, contact section, and fabric filter (Figure 1). The design specifications are listed in Table 2. Upstream of the contact section, the boiler stack gas is cooled to approximately 200°C by a secondary cooling system to protect downstream filters. Calcium hydroxide and steam are then injected into the stack gas in the contact sections in proportion to the quantities of gaseous compounds to be removed, which are mainly sulfur dioxide, hydrogen chloride, and small amounts of hydrogen fluoride. The spent sorbent from the reaction is collected by a fabric filter and sluiced out of the system.

Contact Section

Each contact section consists of three contact tubes each fitted with two flow nozzles, venturi throats, and an impactor grate. Dry calcium hydroxide and steam are injected into the cooled stack gas via binary jets. The calcium hydroxide is introduced on a stoichiometric basis via a metering device which is described in greater detail below. Table 3 shows an average analysis of the sorbent. The volume of steam was set at 0.5 kg steam/kg sorbent based on parametric tests. In the subsequent venturi tubes and impactor grate, the gas, calcium, and steam are swirled so that most of the gaseous components to be removed are bonded to the partially condensing steam and the surface of the calcium particles.

Steam Input. The addition of steam via the two flow nozzles improves the distribution of the calcium in the stack gas flow and also raises the level of abatement for the gaseous components that are to be removed.

The water/steam cycle produces superheated steam at 320°C (608°F) and 32 bar (463 psi). Before it enters the two flow nozzles the steam is reduced to 16 bar (232 psi) and approximately 240°C (464°F). Total steam consumption is restricted to 524 kg (1,153 lb) per hour. During unit startup, steam for stack gas scrubbing is taken from the oil-fired auxiliary steam generator.

Sorbent Metering. The calcium hydroxide silo with a capacity of 150 m^3 (5,300 ft^3) is filled by dumper trucks using a pneumatic conveyor system. The silo extractor unit is designed as a three-part unit in which each section has its own independent, mechanically operated vibrating extractor. A pneumatic metering and conveyor unit is installed beneath the rotary valve of each extractor. The feed pipes to the binary jets are positioned downstream of each metering and conveyor unit. The metering precision is ±5 percent.

To avoid plugging as a result of condensation during pneumatic transport, the pipes are insulated and can be heated electrically. The surfaces of the rotary valves have been specially treated at the points where deposits may form.

Viton B or rubber is used for the gaskets. The straight pipe sections for the pneumatic calcium conveyor are made of mild steel and the hinge fittings of thick-walled plastic. This was the only way to meet the requirements specified for operational life. To avoid static charge buildup in the plastic, ground wires have been inserted which are connected to the adjoining steel pipes.

Filter Pockets

The two pressure shock filters each consist of two vertically aligned rows of filter pockets made of Teflon. The filter pockets are stretched over aperture frames of 1.5 by 1.4m. Table 4 gives the dimensions of the filter assembly.

Filter Cleaning. An eight-bar (116 psi) compressed air system is provided to clean the filters. Only four filter pockets are cleaned at any given time, two from each row. There must be at least four filter pockets operating normally between the two in the row being cleaned to maintain a steady filtering process.

Cleaning with compressed air blasts is controlled in such a way that the pressure drop loss remains constant within a certain operational range.

The pressure drop in a filter depends of course, among other things, on the strength of the filter cake (adhesive calcium layer) and the face velocity of the fabric or gas flow. In this instance, filtering at a pressure loss of 15 mbar (0.22 psi) has proved optimal.

Extraction System. The particles removed from the pressure shock filter are carried by a scraper chain conveyor to a rotary valve and thence removed from the pressure area. The reacted lime is transferred to a silo via a screw mounted traversly to both filters.

OPERATION

Before the chemisorption unit startup, both filters, including both the upstream multiple contact sections and a part of the downstream treated gas duct, are preheated to working temperature. This preheating is achieved by keeping the air in the unit in circulation by a fan and heating it up in a steam-heated heat-exchanger. Measuring points in each of the two filters monitor the temperature and show when the working temperature has been reached.

Sorbent Metering

The concentrations of hydrogen chloride and sulfur dioxide are measured in the treated and untreated gas. Normally, the level of pollution in the untreated gas, the volume of the gas flow, and the stoichiometric ratio determine the amount of sorbent needed.

The measuring devices currently available for gaseous components react sluggishly and cannot therefore detect rapid fluctuations in level. Changes in the flow of stack gas and deviations in the measurements of the metering devices make it even more difficult to adjust to an optimal supply of sorbent without exceeding the permitted concentrations in the treated gas stream. Consequently, values for the treated gas which fall below the maximum permitted levels are superimposed on the sorbent metering. If the permitted levels are exceeded, additional calcium hydroxide is briefly injected into the absorption system.

Operating Results

Since the unit entered into service in 1982, various test series have been taken by SHU and other independent groups. The temperature of the untreated gas normally ranges from 200 to 220°C (390 to 430°F) after the cooler and the level of moisture is 40 to 70 mg/m^3 (STP). The concentrations of SO_2 recorded in the untreated gas have been between 200 and 800 mg/m^3 (70 to 275 ppm). The operating results cover a relatively wide range of 55 to 85 percent removal efficiency as shown in Figure 2. All gas outlet concentrations fell within the range of 90 to 160 mg/m^3 (30 to 55 ppm).

Experimental results at other waste incinerators showed (2) that SO_3 comprises about 1 percent of total sulfur oxide emissions. Comparing the process described here with other dry lime-based processes for sulfur removal, it can be seen that injecting steam in addition to calcium hydroxide considerably increases the SO_2 removal efficiency. In some applications, this process is competitive with wet-scrubbing.

There was no discernable influence on SO_2 removal efficiency due to fluctuations of hydrogen chloride between 500 and 1,750 mg/m^3 (300 to 1,080 ppm) in the untreated gas. The removal efficiency for hydrogen chloride is usually over 90 percent so that levels in excess of 85 mg/m^3 (52 ppm) were rarely found in the treated gas. The hydrogen fluoride in the treated gas was well below 1 mg/m^3 (1 ppm).

In addition to obtaining high removal efficiencies, the program also sought to obtain a high level of sorbent utilization. This is generally defined by the ratio of absorbed mole to Ca mole compared to stoichiometric. Since the present system exhibits fluctuations in the volume of gas and concentrations of pollutants, it is particularly difficult to specify a stoichiometric ratio from the abatement level of the gaseous components.

Accordingly, some analyses were made on the solid matter and the quantity of calcium hydroxide consumed. These analyses showed that approximately 37 percent of the calcium hydroxide had been consumed, which represents a utilization ratio of 1:2.7.

Domestic refuse contains heavy metals such as cadmium, lead, mercury, zinc, vanadium, chrome, etc. which are present in the flue gas and flyash. It is therefore advisable to use a fabric filter for fine particle removal. By cooling down the gas to 200°C (392°F) most of the gaseous heavy metal compounds condense onto the flyash and sorbent which are removed in the fabric filter. The particulate concentration behind the fabric filter is less than 5 mg/m^3.

Cost of Operating Materials

To meet design specifications, the gas scrubbing unit requires 400 kg calcium hydroxide and 200 kg steam per hour. Including transport, the price is DM 150/tonne ($50/tonne) for calcium hydroxide and DM 28/tonne ($9.30/tonne) for steam for power producers. The corresponding costs per hour are DM 60 ($20/tonne) for the calcium hydroxide and only DM 5.60 ($18.70/tonne) for steam which means that the proportion of the costs accounted for by the steam is relatively low (8.5 percent).

Storage of Used Lime

Given the heavy metals and chlorine compounds in the used lime, the operators opted to store it in a special dump near the recycling center. In general, in Germany there are local bylaws covering the dumping of waste products. The main criteria are the proportion of water-soluble components, the tendency of the dumped material to become airborne, the rate of seepage, metal content, and hygroscopicity.

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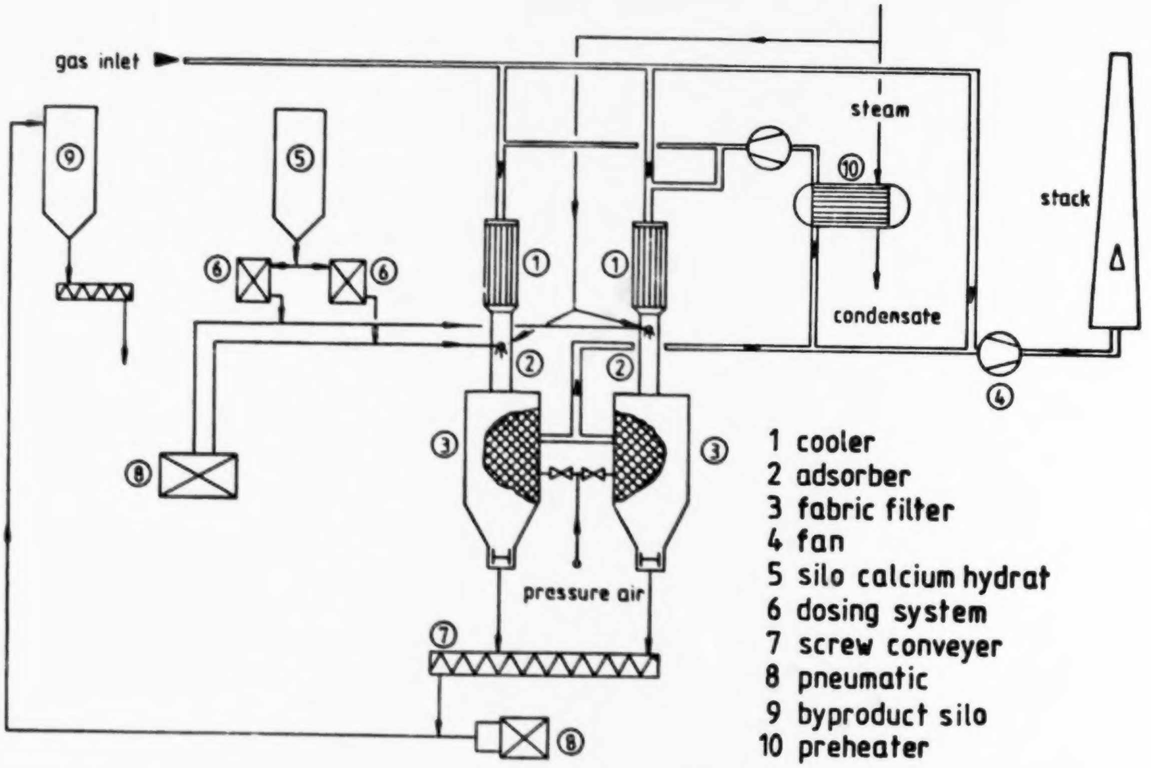
gas inlet
steam
stack
condensate
pressure air
⑨
⑤
⑥
①
②
③
④
⑦
⑧
⑩
1 cooler
2 adsorber
3 fabric filter
4 fan
5 silo calcium hydrat
6 dosing system
7 screw conveyer
8 pneumatic
9 byproduct silo
10 preheater

Figure 1. Schematic of Dry Gas Cleaning at Ruhr Recycling Center

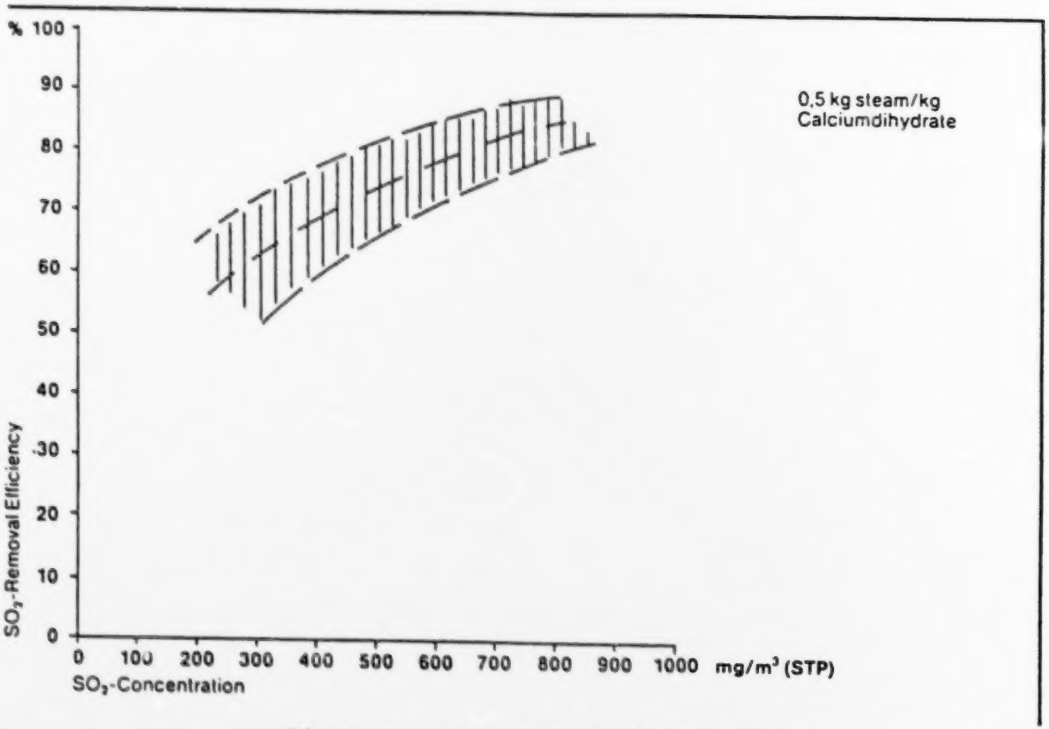

Figure 2. SO_2 Removal Efficiency

Table 1

FLUE GAS DESULFURIZATION PLANTS WITH THE SHU PROCESS

Start up	Client	Application	FGD capacity	Gypsum use
1989/88	RWE Power-Station Neurath	1200 MW lignite-fired boiler	1200 MW	yes
1988	BEWAG, West-Berlin Power-Station Reuter	300 MW coal-fired boiler	300 MW	yes
1987	RWE Power-Station Neurath	900 MW lignite-fired boiler	900 MW	yes
1987	Umlandverband Frankfurt AVA Osthafen	municipal waste incinerator	3 x 71,500 scfm	
1987	Preussische Elektrizitäts-AG Hannover, Power Station Heyden IV	800 MW coal-fired boiler	800 MW	
1987	BEWAG, West-Berlin Power Station Reuter	300 MW coal-fired boiler	300 MW	yes
1985	City Frankfurt MVA Frankfurt Nordweststadt	municipal waste incinerator	2 x 74,600 scfm	
1985	Stadtreinigung Nürnberg	municipal waste incinerator Ofenlinie 4	71,500 scfm	
1985	Von Roll AG Switzerland	municipal waste incinerator	37,500 scfm	(partly absorption)
1984	Kraftwerk Bexbach Verwaltungsgesellschaft mbH Ilse Bayernwerke Energieanlagen GmbH	750 MW coal-fired boiler	260 MW	yes
1984	City Frankfurt MVA Frankfurt Nordweststadt	municipal waste incinerator	2 x 74,600 scfm	
1983	BEWAG, West-Gerlin Power Station Lichterfelde	150 MW oil-fired boiler	150 MW	yes
1983	Saarbergwerke AG Saarbrücken Power Station Weiher III	707 MW coal-fired boiler	125 MW	yes

Table 1 (Concluded)

FUEL GAS DESULFURIZATION PLANTS WITH THE SHU PROCESS

Start up	Client	Application	FGD capacity	Gypsum use
1982	Widmer & Ernst AG Switzerland MVA Schwandorf	municipal waste incinerator	58,500 scfm	
1982	BEWAG, West-Berlin Power-Station Lichterfelde	150 MW oil-fired boiler	150 MW	yes
1982	Widmer & Ernst AG Switzerland RZR Herten/Germany	waste product incinerator	77,000 scfm	- (mainly $CaCl_2$, CaF_2)
1982	Widmer & Ernst AG Switzerland RZR Herten/Germany	municipal waste incinerator	15,500 scfm	- (mainly $CaCl_2$, CaF_2)
1982	Saarbergwerke AG, Saarbrücken Power-Station Völklingen	230 MW coal-fired boiler (fluidized bed)	230 MW	yes
1979	Bayr.Landesamt für Umweltschutz MVA Ebenhausen	special waste incinerator (dry prototype scrubbing)	6,200 scfm	- (mainly $CaCl_2$, CaF_2)
1979	Saarbergwerke AG Saarbrücken Power Station Weiher III	707 MW coal-fired boiler	225 MW	yes
1976	Südwestdeutsche Fernwärme GmbH Saarbrücken	5 t/h municipal incinerator	19,000 scfm	- (mainly $CaCl_2$, CaF_2)
1974	Saarbergwerke AG Saarbrücken Power Station Weiher II	150 MW coal-fired boiler	78,000 scfm	yes
1972	Stadtwerke Solingen MVA Solingen	5 t/h municipal waste incinerator	1,900 acfm	- (mainly $CaCl_2$, CaF_2)

Table 2

DRY ABSORPTION SYSTEM SPECIFICATIONS

Stack gas flowrate	60,000 to 142,000 m^3/h (2.12×10^6 to 5.02×10^6 ft^3/hr)
Temperature of stack gas prior to cooler	483 to 573 K (410 to 572°F)
Temperature of stack gas in filter	443 to 513 K (338 to 464°F)
Concentrations in untreated gas	
$SO_2 + SO_3$	(342 ppm) 1,000 mg/m^3 (as SO_2)
HCl	(920 ppm) 1,500 mg/m^3
HF	(20 ppm) 20 mg/m^3

Table 3

AVERAGE ANALYSIS OF CALCIUM HYDROXIDE

$Ca(OH)_2$	90 to 94 percent
$Mg(OH)_2$	1.4 to 2.2 percent
CO_2	Maximum 2.0 percent
SiO_2	1.0 to 1.7 percent
Al_2O_3	0.45 to 0.65 percent
Fe_2O_3	0.25 to 0.40 percent
Mn_3O_4	0.05 percent
SO_3	0.05 to 0.2 percent
H_2O	23.0 to 24.0 percent
Of which H_2O-free	0.5 to 1.0 percent
Combustion loss	23.0 to 24.0 percent
Particle size 98 percent less than 0.09 mm (about 170 mesh)	
Bulk density	0.4 kg/dm^3

Table 4

DIMENSIONS OF THE FILTER ASSEMBLY

Length	16m (52.5 ft)
Width	8m (26.2 ft)
Height (excluding treated gas duct)	6m (19.7 ft)
Number of filter pockets (total)	816
Number of filter pockets per double row	408
Number of filter pockets per row	204
Total filter surface, approximate	3,000 m^3 (32,300 ft^2)

FLUE GAS DESULFURIZATION BY COMBINED FURNACE LIMESTONE INJECTION AND DRY SCRUBBING

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ABSTRACT

Furnace limestone injection with dry scrubbing offers a viable economic alternative to wet scrubber systems for flue gas desulfurization. The combined technology is most promising from a technical and economic standpoint in application to eastern high-sulfur coals, where SO_2 reduction requirements are most stringent. Combining the two systems can offer required SO_2 reduction in excess of the sole use of either system. Also, combined use of the two systems can represent significant savings in reagent costs over more expensive lime reagent. This is because low-cost limestone is injected into a furnace for calcination to lime and collected lime and ash materials are recycled and employed as the principal reagent in the dry scrubber system.

In pilot plant tests sponsored by the Department of Energy, which investigated the combined process as applied to eastern high-sulfur coals, various furnace injection methods, calcium-to-sulfur stoichiometric ratios (Ca/S), furnace load, and rear-furnace temperatures were studied. Results indicated potentially high SO_2 removal and a cost-effective process with a combined optimized system. These test results, in addition to Babcock & Wilcox research and development experience with the two technologies (separately and in combination), are reviewed in this paper.

INTRODUCTION

Many processes have been developed to remove sulfur dioxide from utility boiler flue gases. One of the more successful processes is the wet scrubber system. Furnace limestone injection and dry scrubbing are also two viable processes for flue gas desulfurization. Like wet scrubbers, their development has grown in response to legislative measures, including the new source performance standards (NSPS) imposed for emissions in 1971. Interest in both systems is increasing in an attempt to develop alternatives to the economic and process-related problems of wet scrubbers.

The limestone injection process injects limestone into the furnace of a utility boiler. Flash calcination occurs to produce lime that, in turn, undergoes reaction with sulfur species in the flue gases. Dry scrubber processes handle flue gases exiting the boiler air heaters through spraying of an alkaline slurry.

Though applied to a wide variety of coals, furnace limestone injection has not yet been proven to reduce SO_2 emissions to NSPS requirements. Dry scrubber systems have successfully been used on western low-sulfur coal for SO_2 removal at NSPS requirements. However, their application to eastern high-sulfur coals have not been proven. Combining the two technologies has the potential to produce flue gas desulfurization at and above the requirements for SO_2 emissions for a complete range of coals. Both systems enhance and complement one another. An optimized combined system with use of recycled ash material as dry scrubber slurry could be both a technical and economic challenger to wet scrubber systems for flue gas desulfurization.

Though similar in some respects to the other, limestone injection and dry scrubbing have developed independently. Babcock & Wilcox (B&W) has been involved extensively in developing both technologies, as well as their combination. A review of B&W research and development programs with results are presented in this paper.

TECHNOLOGICAL REVIEW

Furnace Limestone Injection

The technology of injecting limestone in a furnace for flue gas desulfurization has been under development at B&W for nearly 20 years. Work began in the late 1960s with pilot plant studies followed by full-scale testing in the early 1970s. With the growth of the Environmental Protection Agency's (EPA's) limestone injection multistage burner (LIMB) technology in the early 1980s, B&W again became involved with limestone injection through in-house and contract studies. Before reviewing this development work and discussing technical findings relative to limestone injection technology, an overview of the limestone injection mechanism for furnace limestone injection is presented.

Furnace limestone injection for SO_2 reduction involves limestone ($CaCO_3$) calcination to lime accompanied by lime reaction with sulfur dioxide (SO_2) in an oxidizing atmosphere to form calcium sulfate ($CaSO_4$). This series of reactions is represented as:

$$CaCO_3 \text{ --> } CaO + CO_2 \quad \text{(calcination)} \qquad (1)$$

$$CaO + SO_2 + 1/2\ O_2 \text{ --> } CaSO_4 \quad \text{(sulfation)} \qquad (2)$$

In a reducing atmosphere produced through use of multistage low-NO_x burners, following limestone calcination, sulfur capture proceeds through reaction of hydrogen sulfide (H_2S) and/or carbonyl sulfide (COS) to produce calcium sulfide (CaS) by the equations:

$$CaO + H_2S \text{ --> } CaS + H_2O \quad \text{(sulfide formation)} \qquad (3)$$

$$CaO + COS \text{ --> } CaS + CO_2 \quad \text{(sulfide formation)} \qquad (4)$$

All of these reactions, their rate, degree of completion, and stability of the reaction products, are influenced by stoichiometry (Ca/S molar), limestone composition, burner design, burner operation, temperature at point of injection, flue gas residence time in the furnace, degree of mixing of limestone with flue gases, particle surface area, and CO_2, O_2, and SO_2 gas partial pressure, among others.

Probably the most influential factor for SO_2 adsorption by limestone injection is time and temperature history of the reagent in the flue gases of the furnace. The theoretical dissociation temperature of limestone is 1652°F for ideal conditions, according to Schwarzkopf (1). Limestone calcination at boiler conditions may range up to 2200°F. During reaction, limestone particles expand before decomposition. Calcination begins first at the surface and continues inward, toward the center of the particles, increasing pore volume and surface area but leaving particle volume unchanged. At the completion of calcination, particles achieve the largest pore volume and surface area with unchanged particle volume. This characteristic of lime particles is termed "soft burned" and is the most reactive state of lime (2). Lime particles having a sufficiently small particle size distribution will have the greatest reactivity. As temperature and/or residence time is increased, sintering of the particles begins, also termed "hard burned" or "dead burned," and particle volume, pore volume, and surface area are decreased. At this state, lime particles are least reactive.

Calcined lime reactions with sulfur compounds are also largely dependent on time and temperature. In an oxidizing atmosphere, calcium oxide and sulfur dioxide are most reactive at about 1800°F (3), but reactivity occurs throughout a temperature range from 1400° to 2300°F. At utility boiler furnace conditions, the reaction may occur appreciably between 1800° and 2300°F at 3% excess O_2 and with SO_2 concentrations in the range of 100 to 2500 ppm (4). The oxidizing product, $CaSO_4$, decomposes rapidly as temperature is increased above 2300°F. The cause of this decomposition has been studied by many. Baker and Attar (5) and Dewing and Richardson (6) reported a transformation in crystalline structure that is less stable than the initial structure. It was also determined by Baker and Attar (6) and Besmann, et al. (7) that $CaSO_4$ is more reactive with metal oxides and reducing agent impurities at high temperatures, which serve to hasten decomposition. These impurities are components within the coal fly ash. For reducing atmospheres, lime is most reactive with H_2S and COS at about 2300°F, according to Borgwardt, et al. (8). However, Turkdogan, et al. (9) determined the temperature to be 2000°F for the maximum limiting sulfide solubility of lime in equilibrium with CaS. Like $CaSO_4$, the CaS reaction rate may decrease below 1800°F, and products may decompose above 2300°F.

B&W has studied many of the factors that influence limestone injection; the factors include: additive properties, stoichiometry, injection point, particle size, SO_2 concentration, flue gas oxygen level, particle residence time, catalyst, and additive recycling. They were studied in the late 1960s under contract to the National Air Pollution Control Administration (10). A total of 415 tests using seven coals and 129 different sorbents were run employing a 2- to 20-lb/hr pulverized-coal pilot plant. The results are summarized:

- SO_2 reductions as high as 71% at a 3.8 Ca/S molar stoichiometric ratio were measured. Average values at Ca/S stoichiometric ratios of 1.0 and 2.0 were 21% and 34%, respectively.
- Marl was the most reactive additive at a 3.8 Ca/S stoichiometric ratio, 2300°F injection temperature and 2-second residence time.
- Injection in the mid to upper furnace at about 2500°F was the most effective location.
- Increasing particle surface area up to 2000 cm^2/g improved performance.
- Additive performance increased with increasing SO_2 ppm concentration.
- Decreasing combustion excess air decreased SO_2 removal.

- Furnace slagging decreased with increasing stoichiometric ratio above 2.0 Ca/S.

- Sintering strengths of fly ash mixed with the additive were reduced below those of the fly ash alone at initial tube bank deposition; however, strengths increased with time.

- Precipitator performance was projected to decrease about 20% with additive injection, as observed from high-dust-resistivity measurements.

These results were applied to demonstrate the technology on a full-scale utility boiler in the early 1970s. The program was sponsored by the EPA and involved B&W in the design and installation of a commercial limestone injection system for a 150-MW unit at TVA's Shawnee Station (11). Results of the five-phase effort were discouraging; only about 26% SO_2 removal at a Ca/S stoichiometric ratio of about 2 was achieved at upper furnace injection. In addition, process problems, such as plugging of the boiler reheater and ash hydroveyor, decrease in electrostatic precipitator performance, and changes in the characteristics of waste products handled by the waste disposal system, further complicated efforts. Development of limestone injection technology ceased at B&W following this program.

In the early 1980s, B&W again began studying furnace limestone injection through an in-house program. The process was now being investigated for combined NO_x and SO_x reduction utilizing B&W low-NO_x burners. A B&W in-house study (12) investigated limestone injection locations for SO_2 reduction through the use of the B&W Alliance (Ohio) Research Center (ARC) 6 million-Btu/hr combustion and fuel preparation facility with four dual-register, low-NO_x burners. Test results showed that injection in the upper furnace region provided the greatest sulfur capture.

Presently, B&W is engaged in other furnace limestone injection work. These efforts include pilot plant studies for application to large-scale utility boilers, small (less than 150-MW) utility boiler applications and demonstration, and in-house studies. Along with the in-house programs, B&W is investigating application of the technology to utility boiler units with cyclone burners and to pulverized-coal, low-NO_x units equipped with dry scrubber systems.

Dry Scrubber Systems

The technology of dry scrubbing for flue gas desulfurization has been progressing since the late 1970s. Most investigations have been applied to low-sulfur western coals. B&W's development efforts have advanced since this time on all levels, from pilot plant studies and large-scale demonstration programs to design, engineering, and construction of commercial units. Two commercial units are presently in startup operations.

The dry scrubbing process is fairly straightforward. Process equipment includes a dry scrubber reactor and a particulate collector. Sulfur dioxide removal is facilitated through dispersion of a finely atomized alkaline slurry in the reactor chamber, where it is mixed with a stream of flue gases flowing from the air heaters of a coal-fired utility boiler. As particles in the slurry dry from the sensible heat of the gases, SO_2 molecules diffuse into the thinning water layer of the particles, and sulfur capture occurs. The reaction product is collected or disposed of through the particulate collector, completing the process.

Numerous reagents have been employed in dry scrubbing, including lime, soda ash, trona, and nahcolite. B&W's dry scrubbing experience has centered on lime due, in part, to its availability. Lime (CaO) is used as a reagent in a water slurry, which produces calcium hydroxide $Ca(OH)_2$ through an exothermic reaction. The product reacts with SO_2 in the flue gas to yield calcium sulfite ($CaSO_3$) as the final principal product:

$$CaO + H_2O \dashrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + SO_2 \dashrightarrow CaSO_3 + H_2O$$

As the lime particles in the flue gas flow through the dry scrubber reactor, the rate of reaction decreases as the particles dry.

Following the drying process, when the particles are dried to their equilibrium moisture content, the rate of reaction is greatly decreased. Following the dry scrubber reactor, lime particles in the flue gases are collected in the particulate collector. Additional reactions occur in the particulate collector through direct contact as flue gas flows through ash or near the unreacted lime deposits.

A number of variables influence the dry scrubbing process performance technically and economically. These include CaO/SO_2 stoichiometric ratio, use of recycled materials, reactor approach to saturation temperature, SO_2 concentration, reagent type, and reactor inlet temperature, among others. All of these variables play important roles in optimizing the system for application to low- and high-sulfur coals.

Stoichiometric ratio (the quantity of reagent used in the system) largely influences SO_2 removal. High stoichiometric ratio aids SO_2 capture. In addition, operating the dry scrubber at a high relative humidity enhances sulfur capture. Sulfur capture may also be enhanced through use of ash recycle, which increases reagent utilization by making use of unreacted calcium hydroxide that has passed through the reactor; it also increases the utilization of coal ash alkalinity.

B&W became involved with the dry scrubbing concept in late 1977. At that time, Basin Electric Power Corporation was soliciting bids for a dry scrubber system at its Antelope Valley Unit No. 1. The fuel for the plant was a low-sulfur coal that had a highly alkaline fly ash.

To qualify as a bidder for the Basin project, B&W had to build and operate a pilot facility to demonstrate the technology. The pilot unit was located at Basin Electric's Neal Station in Velva, North Dakota and was sized to handle 8000 ACFM of flue gas. The pilot featured a horizontal-flow reactor. Lime slurry was introduced into the dry scrubber through a Y-jet pneumatic atomizer. Operation of this pilot began in June 1978 and continued for approximately one year.

The results from this pilot work were very encouraging and resulted in B&W obtaining a contract from Basin Electric for its new Laramie River No. 3 Station. During the Velva test program, two important system parameters were observed to have a profound influence upon the dry scrubber performance (13). First, as the exit gas temperature from the dry scrubber was made to approach the adiabatic saturation temperature of the gas, SO_2 removal improved substantially. Secondly, the influence of alkaline fly ash on SO_2 removal was observed.

After completing the tests at Neal Station, a large-scale demonstration unit capable of handling 120,000 ACFM of flue gas was constructed at Pacific Power and Light's Jim Bridger Station in Rock Springs, Wyoming. This unit initially began operation in the summer of 1979 and operated until December 1980. The unit was designed with completely automated controls and included a baghouse and precipitator.

The main function of this unit was to demonstrate the scaleup and controllability of the process in a utility environment. This demonstration included long-duration runs, including automatic load following (14). The most significant result of the tests was that the high alkalinity of Laramie River coal (sub-bituminous) enabled capture of at least 65% SO_2 with water spray.

A second pilot facility that has the flexibility for changing fuels and testing a wide range of variables was constructed at B&W's Alliance Research Center. This 1,500-ACFM unit began operation in July 1979. The unit is connected to a 5×10^6-Btu/hr combustor that is designed to burn coal, oil, or gas. The pilot has been used for testing many different coals, with sulfur ranges from 0.4% to 2.2%. These coals also represented a wide range of ash alkalinities. Testing also has been conducted using oil and gas (15).

B&W has correlated the results of its two pilot units and large-scale demonstration unit. This gave B&W the ability to perform tests in a tightly controlled manner and then to scale up the results based on the 1,500 ACFM pilot and the 120,000 ACFM demonstration unit.

As a result of these development efforts, B&W sold two commercial systems to the utility market. The first unit (580 MW) was sold to the Basin Electric Power Corporation for its Laramie River No. 3 Station. The second unit (447 MW) was sold to the Colorado Ute Electric Association for its Craig No. 3 Station. The first unit is equipped with an electrostatic precipitator, and the second unit with a baghouse. Both systems burn low-sulfur western coal. A schematic of the dry scrubber design of these units (with plenum arrangement) is shown in Figure 1.

Presently, B&W is engaged in pilot and full-scale testing to optimize the dry scrubbing process. A recent study (16) characterized dry scrubber technical and economical potential for eastern high-sulfur coals. The pilot test program sponsored by the Department of Energy (DOE) under Contract DE-AC22-81FE-17056 ("Eastern Coal Spray Dryer Evaluation") investigated the various dry scrubber system variables as affected by high-sulfur coals. It was concluded from the program that satisfactory SO_2 removal for these coals required use of a fairly high quantity of reagent, dry scrubber operation at low approach to saturation, and use of recycled ash material. The study suggests that the use of limestone injection with ash recycle would increase the economic attractiveness of dry scrubber systems compared to wet scrubber systems for flue gas desulfurization of these high-sulfur coals.

DRY SCRUBBING AND LIMESTONE INJECTION FOR EASTERN HIGH-SULFUR COAL

Overview

The potential drawbacks in using the dry scrubber for units burning high-sulfur coal are both technical and economical. The high-sulfur coals generally have very low-alkaline fly ash, requiring more reagent to be used in the dry scrubber. Also, the sulfur dioxide removal requirements are more stringent (90% removal required). The dry scrubbing process has a built-in limitation for the amount of reagent slurry that can be sprayed into the flue gas stream. This spraying capacity is controlled by the available heat in the incoming flue gas that can be used for evaporation of the moisture in the slurry. Also, as the sulfur loading in the gas increases, it becomes necessary to increase the solids concentration of the slurry. Limits exist regarding the slaking, pumping, and atomizing of viscous slurries.

From an economic standpoint, the cost of reagent material can be a very important parameter; lime is considerably more expensive than limestone. For low-sulfur coals, the quantity of reagent required for dry scrubbing is low. For high-sulfur coals, however, where the reagent cost can be a dominant factor, the relative difference in costs between lime and limestone can be the dominant factor in present application of dry scrubber technology to eastern coals.

Furnace limestone injection in combination with dry scrubbing of eastern bituminous coal is one means of increasing the economic attractiveness of dry scrubber systems. This approach was examined by B&W. The first study (17) was an exploratory examination of this concept. A 2.3%-sulfur coal was fired; limestone was injected into the furnace at various stoichiometric ratios (Ca/S). Recycled material was used as slurry in the dry scrubber at various stoichiometric ratios (Ca/SO_2). Overall SO_2 removal was as high as 86%.

The second study was completed by B&W under DOE Contract DE-AC22-81FE 17056 (16) and was geared toward investigating dry scrubber system variables and system design options to expand effectiveness for eastern coals. Furnace limestone injection was evaluated as a design option to determine whether reagent requirements would be decreased by furnace calcination of limestone to lime. The lime was then entrained in the flue gases flowing to the dry scrubber. We anticipated that reagent requirements at the dry scrubber would be reduced because of SO_2 capture in the furnace. A 3.1%-sulfur coal was used. Various locations, stoichiometric ratios, and flue gas temperatures were studied in the furnace. An atomized water spray was used in the dry scrubber.

Test Apparatus

B&W's 1500-ACFM dry scrubber pilot (Figure 2) was used for the DOE and in-house tests. Three main components make up the system: the basic combustion test unit (BCTU), the dry scrubber, and the baghouse particulate collector.

Pulverized coal stored in a 5-ton hopper was screw fed into the primary air line, where it was transported to the 5 million-Btu/hr BCTU, as shown in Figure 3. Coal was fired using a low-NO_x burner operated in a low-NO_x mode, which produced a long, lazy flame. Limestone was metered to the furnace at a rate corresponding to the particular stoichiometric ratio desired via a 160-lb/hr Vibra screw feeder. An eductor was used to aspirate limestone flow for furnace injection. In the furnace, limestone rapidly calcined to lime as it mixed with the flue gases. SO_2 capture was facilitated as flue gas, lime, and ash matter flowed through the BCTU furnace. The gases encountered an approximate 1-second residence time in the furnace at temperatures ranging from about 2500°F at the hottest portion of the flame to near 1500°F at the furnace exit.

Flue gases exiting the furnace were routed to the dry scrubber (Figure 4). A portion of gases was sent through a water-cooled, counter-current heat exchanger to maintain a 300°F dry scrubber inlet temperature. Cooled flue gases entered the dry scrubber through a windbox plenum, where a perforated plate distributed the gas for even flow through the registers of the Turbo-Diffuser slurry atomizer assembly. The Turbo-Diffuser, a B&W trade name for the slurry atomizer assembly, features a pneumatic atomizer that disperses slurry flowing through an inner tube by pressure of compressed air flowing through an outer tube. Flue gas was directed around the atomizer, where tangentially located vanes in a register imparted a swirl to provide adequate mixing of gas with atomized slurry.

Slurry was produced by a 1000-lb/hr-capacity paste slaker equipped with a 20-mesh screen to remove large unslaked lime particles and impurities. Lime from the paste slaker was discharged into the main product tank, where water was added to adjust slurry to the appropriate percentage of solids. For ash recycle slurries, ash collected from the dry scrubber and baghouse was manually dumped into the tank. Slurry was pumped to the Turbo-Diffuser, where supplemental water was added to the Turbo-Diffuser to maintain appropriate dry scrubber approach to saturation temperature. Approach to saturation temperature is defined as the difference in temperature between the dry scrubber outlet temperature and the adiabatic saturation temperature of the gas. Inside the dry scrubber, flue gas SO_2 diffused into the lime particles, resulting in SO_2 capture. Heavy ash matter fell out into the dry scrubber hoppers for disposal or recycle, and lighter ash matter was carried with the flue gases to the baghouse and cyclone.

The 500-ACFM baghouse removes particulate matter from one-third of the flue gas and is equipped with an in-line heater for reheating flue gas before entering the baghouse. This ash is collected on the inside of 16, 10-foot-long x 4-1/2-inch-diameter woven bags with three anticollapse rings. Additional SO_2 capture occurred as flue gas SO_2 flowed through the inside of the bags contacting accumulated unreacted lime and ash matter. A cyclone separator with the capability of handling 100% of the flue gases collects particulates from the remaining two-thirds of the flue gases. Flue gases from both particulate collectors were then directed to the 5000-ACFM induced-draft fan and then discharged to the atmosphere through the stack.

Test Description

Two separate studies were conducted: one funded by DOE (16), and one funded internally by B&W (17). The DOE limestone injection/dry scrubbing tests examined two furnace injection schemes (primary and secondary) and three stoichiometric ratios (1.0, 2.0 and 3.0). Rear-furnace temperatures of 1800°, 2000°, and 2200°F were studied by varying the firing rate at an approximate 3% excess O_2. Note that the BCTU furnace has no provision for measuring furnace exit gas temperature; therefore, temperatures were measured through a viewport at the rear of the furnace. Simultaneous to the BCTU limestone injection, water spray was used in the dry scrubber, with an approach to saturation temperature averaging 37°F. Baghouse performance was not monitored in the tests.

The in-house study considered only primary injection mode, with a 3.0 and 4.0 furnace stoichiometric ratio. A 1.6 and 2.8 stoichiometric ratio, respectively, was studied in the dry scrubber employing ash recycle at a 25°F approach to saturation temperature.

In the primary injection mode, limestone was mixed with coal and primary air in the feed pipe. The mixture was injected into the furnace through the low-NO_x burner. Injecting limestone in this manner created two conditions relative to reagent reactivity:

- The greatest degree of mixing of calcined lime and flue gas SO_2
- The longest time period in the highest temperature zones of the furnace.

The main concern expressed for this injection scheme is decreased reagent utilization as a result of the latter. Since sulfur capture reaction is time and temperature sensitive (though mixing may be adequate), lime reactivity may be reduced due to dead burning (loss of lime particle surface area) and dissociation of product.

Secondary injection for the DOE tests introduced limestone through a side viewport downstream from the burners and in a cooler temperature zone. The cooler temperatures reduce the opportunity of calcined lime dead burning and product dissociation. Although flue gas furnace residence time was appropriate, mixing of reactant SO_2 and lime may have been reduced. The proper injection location was arrived at through preliminary shakedown tests, including high-velocity traverse (HVT).

These tests were conducted to determine a limestone injection location along the length of the BCTU furnace that would correspond to a 2000°F injection temperature. A typical furnace temperature profile for 4 million Btu/hr at 3% furnace excess O_2 and a 2000°F rear-furnace temperature is shown in Figure 5. Viewport No. 2 on both sides of the BCTU furnace was designated as the secondary injection site. The secondary injection ports are located on both sides of the periphery of the flame, far enough upstream to facilitate mixing and produce an appropriate residence time. This injection point is about 2.5 feet from the burner and 14 inches into the furnace and affords SO_2 and CaO a 1.3-second residence time in the furnace, assuming plug flow.

Of interest in this figure is the temperature and shape of the flame produced through the low-NO_x burner. The flame is fairly long and narrow, exhibiting cooler temperatures of 2300°F or less. The core of the flame occurs downstream of the burner along Port No. 2. This configuration of the flame reduces NO_x formation, while the cooler temperatures benefit limestone calcination and sulfur capture.

Test Results and Conclusions

The results and operating conditions of the DOE tests are tabulated in Table 1. A representation of the furnace SO_2 removal results (Figure 6) indicates a general increase in SO_2 removal with stoichiometric ratio. The dry scrubber results exhibit a generally unchanging trend with furnace stoichiometric ratio. Sulfur dioxide removal in both unit operations was much lower than anticipated. Overall SO_2 results are shown in Figure 7. The in-house study results (tabulated in Table 2 and shown in Figure 8) indicate increased dry scrubber SO_2 removal with the use of recycle slurry.

Primary injection tests of the DOE study, all run at 4 million Btu/hr furnace load, 2000°F rear-furnace temperature, and 3% excess O_2, produced a high of 20% SO_2 removal in the furnace at the high 3.0 Ca/S stoichiometric ratio. With water spray in the dry scrubber at a 37°F approach to saturation temperature, SO_2 removal indicated a slight decrease with stoichiometric ratio, averaging 8%. The difference in dry scrubber SO_2 removal for these tests can be considered negligible. In the overall system, a high of 24% SO_2 removal was achieved at the 3.0 stoichiometric ratio.

The secondary injection tests run at the various furnace operating conditions produced somewhat more representative results. The highest furnace SO_2 removal of 26% was attained at reduced load (3 million Btu/hr), low rear-furnace temperature (1800°F), a high furnace stoichiometric ratio (3.0 Ca/S), and 3.0% excess furnace O_2. The best dry scrubber removal of 18% was obtained using water spray for the reduced-load tests. At full load and a 2000°F rear-furnace temperature, furnace SO_2 removal increased with stoichiometric ratio (as in the primary injection test) to 22% at 3.0 stoichiometric ratio. An average dry scrubber SO_2 removal of 13% was determined for these tests with water spray. The higher 2200°F rear-furnace temperature tests produced an average 20% furnace removal at all furnace stoichiometric ratios with no apparent trend. Sulfur dioxide removal in the dry scrubber for these tests also exhibited no apparent trend, averaging 10% SO_2 removal with use of a water spray. For the overall system, the reduced-load tests produced a high (39%) SO_2 removal, and the full-load tests averaged near 28% removal.

The in-house study considered primary limestone injection for use with either ash recycle or water spray in the dry scrubber. Furnace SO_2 removal did not exhibit a dramatic increase with stoichiometric ratio but averaged 24% removal. In these tests using 3.0 Ca/S furnace stoichiometric ratio and full load, dry scrubber SO_2 removal did not increase above 12% with water spray, even with a low 25°F dry scrubber approach to saturation temperature. With use of recycle slurry (rather than water spray) at a 1.6 CaO/SO_2 stoichiometric ratio, dry scrubber SO_2 removal increased to 22%, producing 40% removal overall. At a higher furnace stoichiometric ratio of 4.6 Ca/S, dry scrubber removal with water spray increased to 43% SO_2 removal. With the use of recycle slurry at 2.8 Ca/S stoichiometric ratio, however, the dry scrubber achieved an 82% removal with an 86% removal for the system. This study illustrates the influence of the use of ash recycle in the dry scrubber on SO_2 removal.

Overall furnace and dry scrubber removal employing water spray were low. With the use of water in the dry scrubber, the alkalinity for SO_2 removal was obtained from entrained particulates in the flue gases. These particulates require slaking to fully activate the alkalinity. Furnace removals were low for both studies, apparently due to a larger-than-optimal limestone grind size, 70% - 200 mesh. This large grind size of the limestone produced a reduction in particle surface area on calcination. With exposure to furnace heat, additional surface area is lost, limiting calcined lime reactivity. For the primary injection test, in addition, the long residence time in the high-temperature region of the furnace further reduced lime reactivity. The problem of low SO_2 removal for the secondary tests was most likely due to insufficient mixing of calcined lime and flue gas SO_2 in addition to large grind size. In the dry scrubber, SO_2 removals were low largely due to ash dropout in the piping and heat exchanger between the furnace and the dry scrubber. The near 70% loss of furnace carry-over ash with unreacted lime eliminated much of the reagent required for SO_2 capture. As a result, dry scrubber SO_2 removal did not rise above 18%.

In conclusion, the two studies (DOE and in house) together revealed a number of technical advantages of the combination of both systems (limestone injection with dry scrubbing for flue gas desulfurization) over either system separately.

- The DOE study indicated limestone injection away from the burners downstream of the furnace produced somewhat higher SO_2 removal in the furnace than limestone injection with the coal through the burners. System optimization is required to increase SO_2 removal.

- Also shown through the DOE tests is a direct dependence of furnace SO_2 removal on furnace stoichiometry. As the furnace stoichiometric ratio is increased, furnace removal increases.

- The B&W in-house study revealed an increase in dry scrubber SO_2 removal, with recycle slurry at high stoichiometric ratios.

- The in-house study also indicated that the combination of both systems (limestone injection employing a high stoichiometric ratio with dry scrubbing using recycled slurry) improves overall SO_2 removal above the use of either system separately.

- Both studies indicate an optimized furnace limestone injection and dry scrubber system can produce SO_2 removal for eastern high-sulfur coals approaching -- if not surpassing -- the 1979 EPA new source performance standards (NSPS) for high-sulfur coals. This system would include use of appropriate grind size and a suitable mechanism for mixing limestone with flue gases away from the burners and a dry scrubber employing recycle slurry. Neither system separately can achieve the 70% to 90% SO_2 reduction requirement without use of a large quantity of reagent.

Use of recycled slurry produced from inexpensive limestone used in furnace injection decreases -- if not eliminates -- use of lime or other expensive dry scrubber reagents. In economic terms, we anticipate that this use of limestone as a reagent decreases reagent costs for eastern coals and equates -- if not reduces -- capital and operating cost compared to that of wet scrubber systems for these coals (15).

FUTURE WORK

The combination of limestone injection with dry scrubbing for flue gas desulfurization holds much promise as an alternative to wet scrubber systems. B&W realizes the potential as well as the implications of the combined system. Therefore, B&W has planned in-house studies and will solicit funding for programs designed to investigate the intricacies of the technology from the laboratory scale to the utility boiler scale. Of particular interest to B&W is application to units equipped with cyclone burners. Presently, B&W is engaged in a test program to study the combined process in a large-scale utility boiler.

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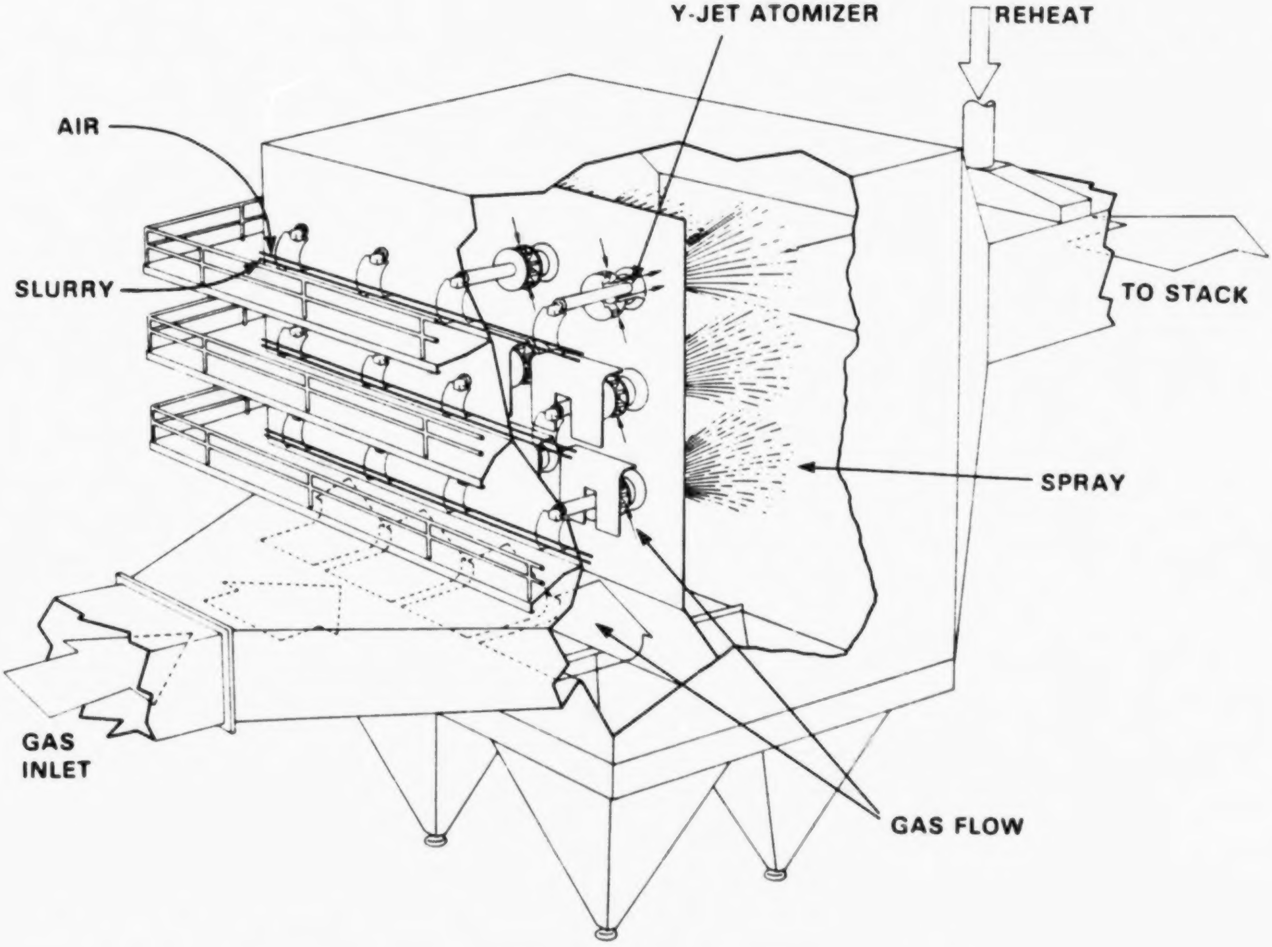

Figure 1. Dry scrubber reactor plenum arrangement

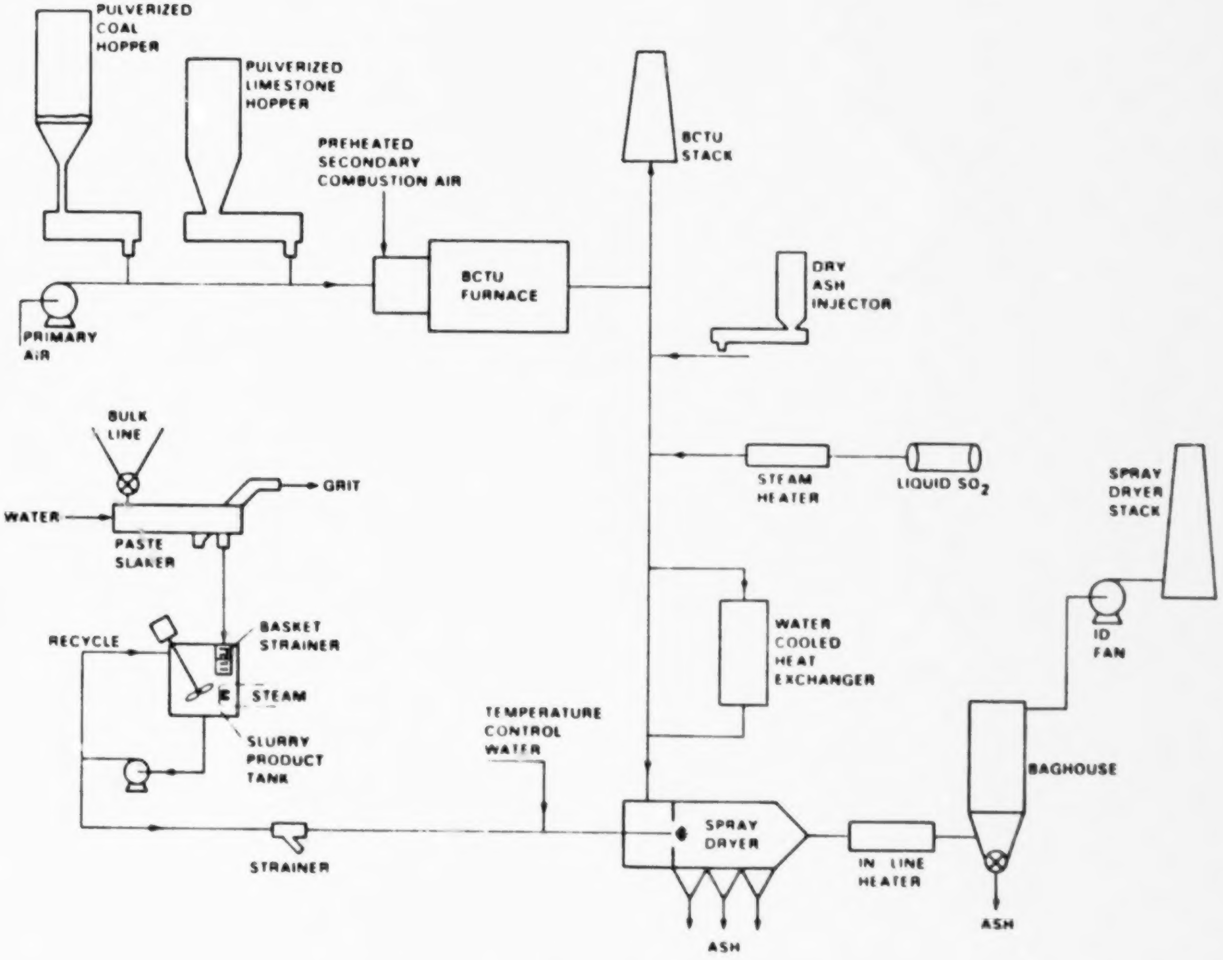
PULVERIZED COAL HOPPER
PULVERIZED LIMESTONE HOPPER
PREHEATED SECONDARY COMBUSTION AIR
BCTU STACK
BCTU FURNACE
PRIMARY AIR
DRY ASH INJECTOR
BULK LINE
GRIT
WATER
PASTE SLAKER
STEAM HEATER
LIQUID SO_2
SPRAY DRYER STACK
RECYCLE
BASKET STRAINER
STEAM
SLURRY PRODUCT TANK
WATER COOLED HEAT EXCHANGER
ID FAN
TEMPERATURE CONTROL WATER
BAGHOUSE
SPRAY DRYER
STRAINER
IN LINE HEATER
ASH
ASH

Figure 2. 1500-ACFM dry scrubber pilot

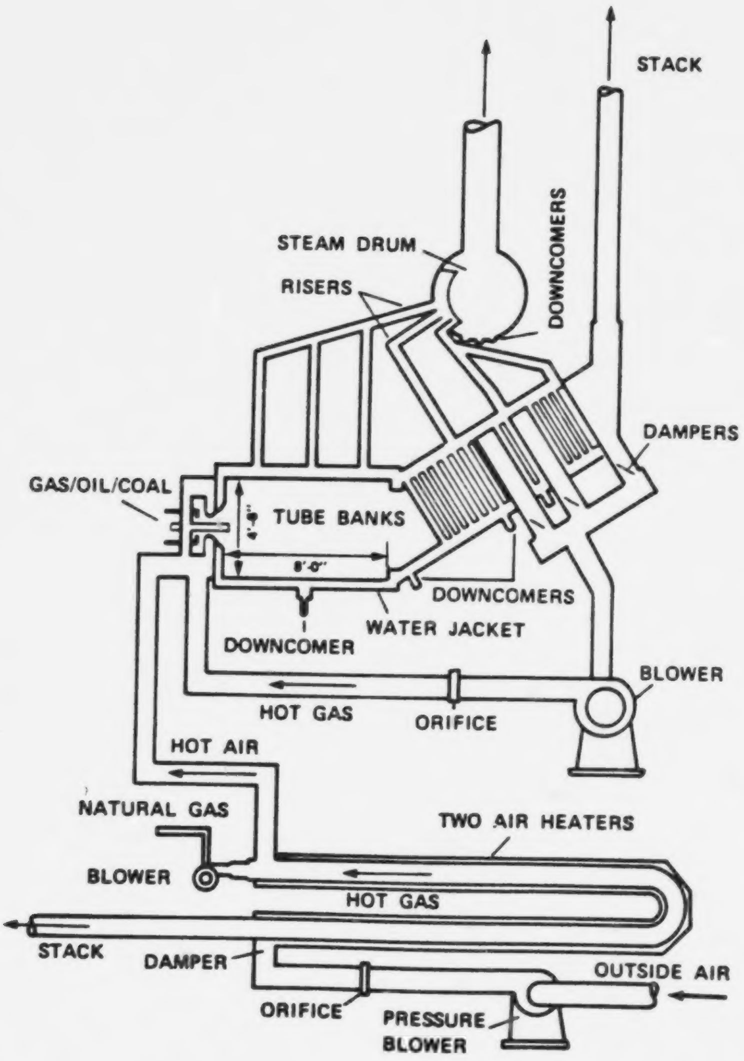
STACK
DOWNCOMERS
STEAM DRUM
RISERS
DAMPERS
GAS/OIL/COAL
TUBE BANKS
8'-0"
DOWNCOMERS
WATER JACKET
DOWNCOMER
BLOWER
HOT GAS
ORIFICE
HOT AIR
NATURAL GAS
TWO AIR HEATERS
BLOWER
HOT GAS
STACK
DAMPER
OUTSIDE AIR
ORIFICE
PRESSURE BLOWER

Figure 3. Basic combustion test unit (BCTU)

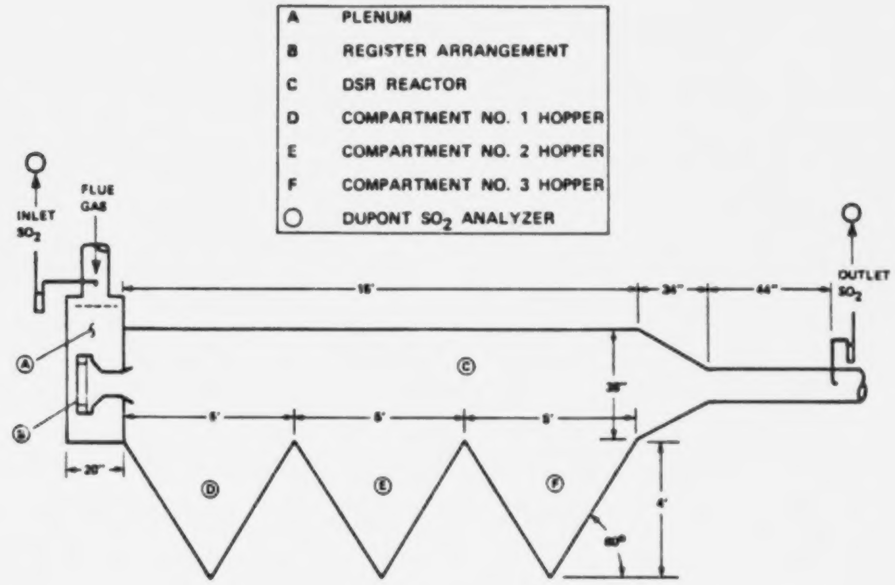
A PLENUM
B REGISTER ARRANGEMENT
C DSR REACTOR
D COMPARTMENT NO. 1 HOPPER
E COMPARTMENT NO. 2 HOPPER
F COMPARTMENT NO. 3 HOPPER
○ DUPONT SO2 ANALYZER
INLET SO2
FLUE GAS
OUTLET SO2
16'
34"
44"
38"
5'
5'
5'
20"
4'
60°
A
B
C
D
E
F

Figure 4. Dry scrubber dimensions

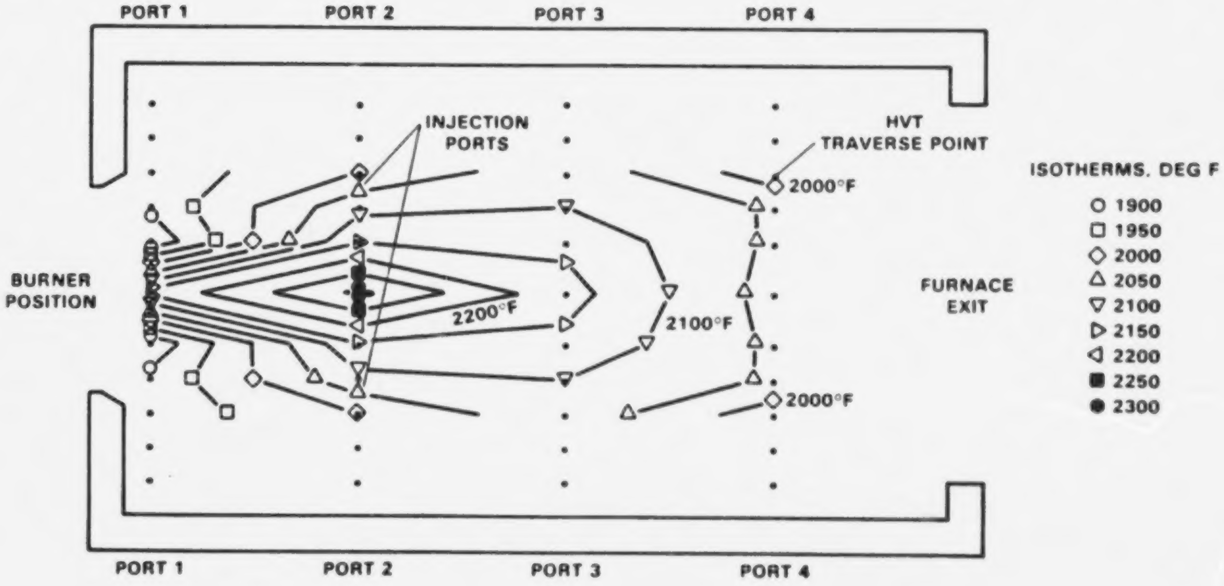

Figure 5. Furnace temperature profile; 4 million-Btu/hr load, 3% O_2, 2000°F FEGT, low-NO_x, dual-register burner

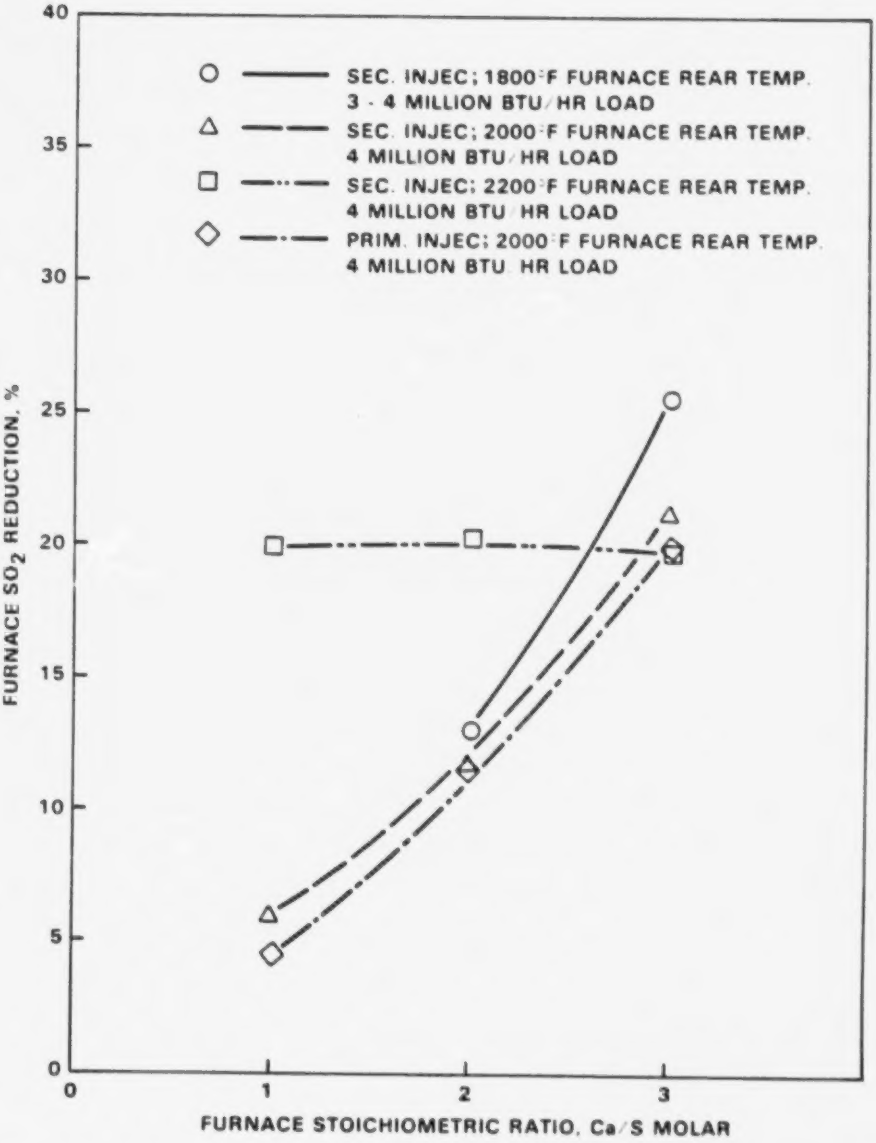

Figure 6. Furnace SO_2 reduction results -- DOE furnace limestone injection test

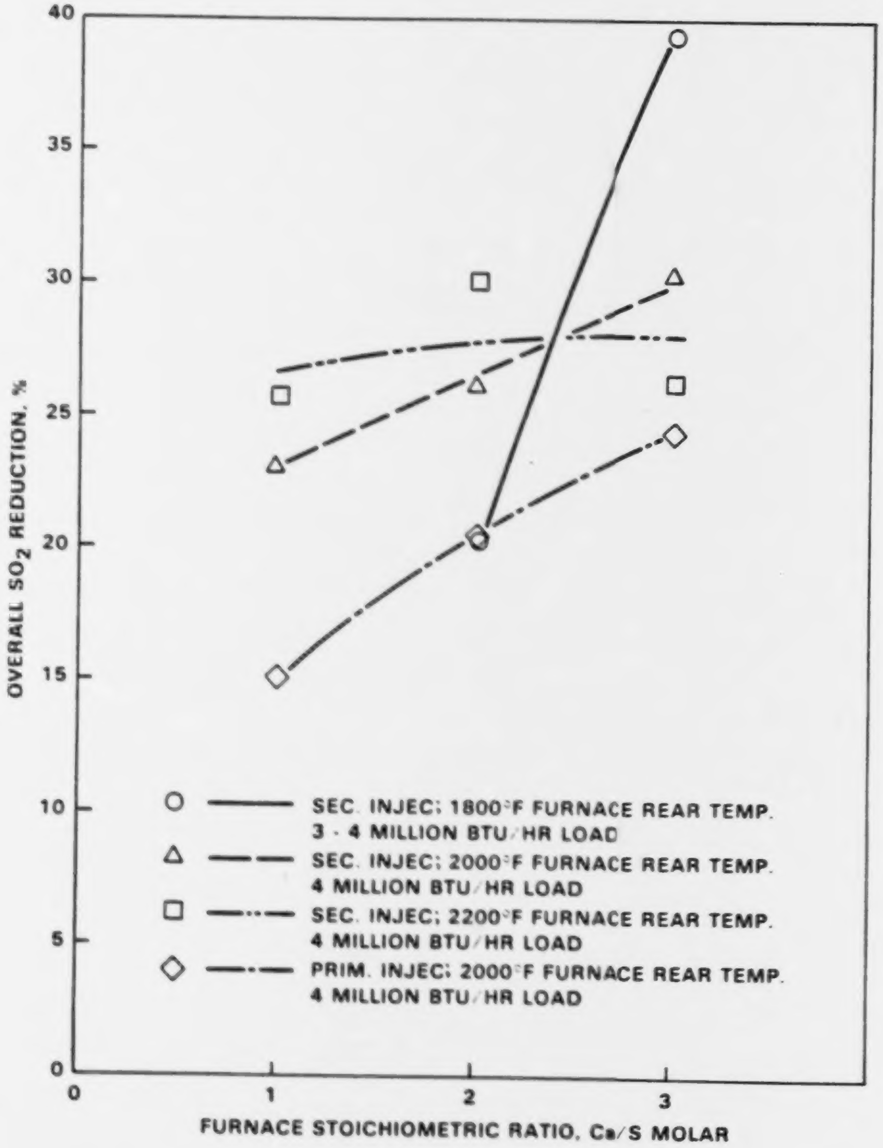

Figure 7. Overall SO_2 reduction results -- DOE furnace limestone injection test

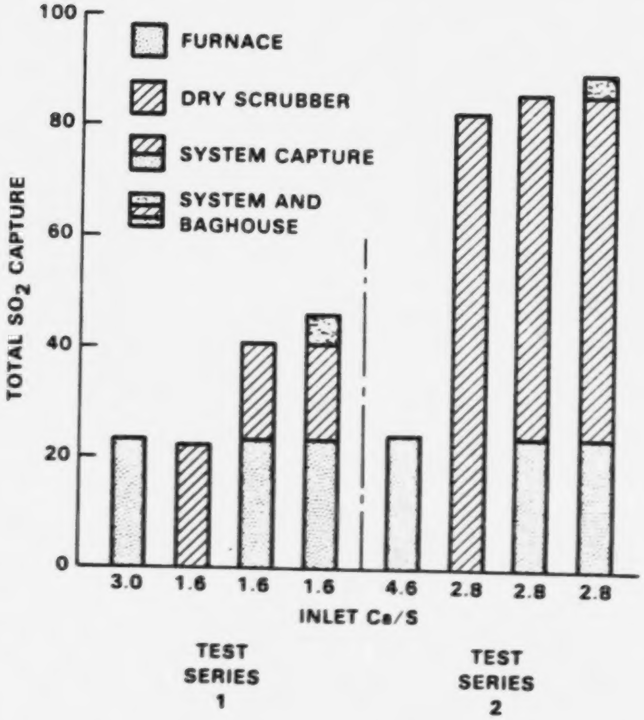

Figure 8. SO_2 removal -- B&W in house study

Table 1

RESULTS OF DOE LIMESTONE INJECTION TESTS

		Furnace				SO_2 Removal (%)		
Run No.	Injection Method	Load (MkB/hr)	O_2 (%)	Port 4 Temp (°F)	Stoichiometry (Ca/S)	Furnace	Dry Scrubber	Overall
212(1)	Sec.	3	3.0	1800	3	26.0	17.3	38.8
213	Sec.	2	4.0	1800	2	13.6	17.8	20.4
215(2)	Sec.	4	3.0	2000	3	22.4	10.5	30.6
216	Sec.	4	3.0	2000	2	13.3	15.9	27.1
217	Sec.	4	3.0	2000	1	7.3	11.9	23.6
218(3)	Sec.	4	3.0	2200	3	19.3	10.0	27.4
219	Sec.	4	4.3	2200	2	20.6	11.8	30.0
220	Sec.	4	3.7	2200	1	19.9	8.1	26.4
221(4)	Prim.	4	2.8	2000	3	20.0	5.1	24.1
222	Prim.	4	2.75	2000	2	13.6	8.8	21.2
223	Prim.	4	3.0	2000	1	4.1	10.6	15.0

NOTES FOR DRY SCRUBBER OPERATING CONDITIONS:

1. Avg. operating conditions, Runs 212 and 213:
   Approach temp -- 37°F
   Inlet temp. -- 308°F
   Residence time -- 9.79 sec

2. Avg operating conditions, Runs 215 - 217:
   Appraoch temp -- 38°F
   Inlet temp -- 304°F
   Residence time -- 11.04 sec

3. Avg. operating conditions, Runs 218 - 220:
   Approach temp -- 35°F
   Inlet temp. -- 309°F
   Residence time -- 10.50 sec

4. Avg operating conditions, Runs 221 - 223:
   Appraoch temp -- 37°F
   Inlet temp -- 309°F
   Residence Time -- 10.69 sec

Table 2

OPERATING CONDITIONS AND TEST RESULTS -- B&W IN-HOUSE STUDY

	TEST SERIES 1	TEST SERIES 2
Operating Conditions		
Coal Feed Rate (lb/hr)	325	325
Sulfur in Coal (%)	2.3	2.3
Furnace:		
- Temperature (°F)	2550	2530
- Ca/S Ratio	3.0	4.6
Dry Scrubber:		
- Inlet Temperature (°F)	314	425
- Outlet Temperature (°F)	151	160
- Approach-to-Saturation Temperature (°F)	25	25
- Ca/S Ratio	1.6	2.8
- Inlet Dust Loading		
(lb/acfm)	2.41	3.13
(% Theoretical)	(30.5)	(27.5)
Slurry Solids (%)	21.1	19.5
Test Results		
SO_2 Removal (%)		
- Furnace	23	24
- Dry Scrubber (With Water Only)	12	43
- Dry Scrubber (With Recycle Slurry)	22	82
- System (With Recycle Slurry)	40	86

PILOT EVALUATION OF COMBINED SO_2 AND PARTICULATE REMOVAL ON A FABRIC FILTER

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ABSTRACT

The injection of calcium compounds into the flue gas upstream of a fabric filter is under evaluation as a means of simultaneous SO_2 and particulate emission control. Pilot tests are being conducted on a 100 acfm slipstream from a pulverized coal fired boiler burning 3% sulfur coal. Water injection, steam injection, and heat extraction are used to condition the flue gas to desired temperatures and humidities. SO_2 removal occurs in the flue gas ductwork, in the expansion plenum upstream of the fabric filter, and across the fabric dustcake. Tests with pressure hydrated dolomitic lime indicated higher SO_2 removal as the flue gas temperature approached the saturation temperature. Fifty percent SO_2 removal was observed at an approach temperature of 25°F when the sorbent was injected at a calcium-to-sulfur ratio of 1:1 and up to 80% SO_2 removal at a calcium-to-sulfur ratio of 2.9:1.

OBJECTIVE

A pilot test facility was built at the Scholz power station of Gulf Power Company in Sneads, Florida, to perform proof-of-concept tests of a combined SO_2 and particulate control process involving injection of calcium-based alkali compounds upstream of a fabric filter. The 100 acfm facility operated on a flue gas slipstream from a pulverized coal-fired boiler burning 3% sulfur coal. Calcium based sorbents, including pressure hydrated dolomitic lime (the majority of tests used this lime), pressure hydrated high calcium lime, conventionally slaked hydrated lime and quick lime were evaluated. In addition to performing comparative tests with the different sorbent materials, an assessment of flue gas parameters with respect to promotion of SO_2 removal efficiency was performed . These parameters included moisture content, flue gas temperature, temperature difference between dew point and actual flue gas temperature (commonly referred to as approach temperature), and relative humidity. A further objective was to quantify SO_2 removal in the various portions of the pilot plant, including the ductwork, the inlet plenum to the fabric filter, and the fabric dustcake.

PROCESS DESCRIPTION

A schematic diagram of the all-dry SO_2 removal process is shown in Figure 1. In this process pulverized sorbent material is fed into the flue gas between the air preheater and baghouse. The reagent can react with SO_2 in the short residence time (1 sec) ductwork, the long residence time (1 min) inlet plenum to the fabric filter, or on the fabric filter dustcake where intimate contacting between SO_2 and reagent can occur. The flue gas was conditioned through steam injection, water injection and/or heat extraction upstream of the fabric filter. By injecting steam at flue gas temperature the moisture content of the flue gas was increased without affecting approach temperature or relative humidity significantly. Heat extraction allowed reduction of the approach temperature and increased the relative humidity without changing the absolute moisture content. The injection of water served two purposes: it increased the absolute moisture content, and dropped the flue gas temperature as a result of latent heat conversion in the evaporation process. This lowered the approach temperature and increased the relative humidity.

TEST FACILITY

Figure 2 shows a schematic diagram of the 100 acfm slipstream facility. The sorbent feed system consisted of a screwfeeder mounted on an electric scale for feedrate determination. Sorbent was fed into a prototype deagglomerator, from which it was carried out by a 1 cfm gas flow and injected through a dispersion nozzle into the 8-in. diameter duct. The water injected into the flue gas was metered through a rotameter, preheated to enhance evaporation (thus minimizing problems associated with wetting the duct walls), and sprayed through an ultrasonic atomizer into the flue gas. Steam was electrically generated, superheated to the desired temperature, and metered through an orifice. One acfm slipstream off of the 100 acfm duct was routed through a heated filter (Fabric Filter Sampling System) to simulate the fabric filter.

TESTS AND RESULTS

In Figure 3 an SO_2 profile throughout the system for a typical test is shown. The time scale on the abscissa represents the residence time of the sorbent after injection. The SO_2 concentration in ppm at any given location is shown as the ordinate. In this example, the SO_2 concentration upstream of the sorbent injection was 2400 ppm. Sorbent was injected at a reagent molar ratio of Ca/S = 1:1. Water was injected into the flue gas 8 feet (2 sec) downstream of the sorbent injection location. This dropped the temperature from 300 to 210°F. The SO_2 concentration was reduced to 2000 ppm. Using heat extraction the temperature upstream of the filter dropped to 135°F. The SO_2 concentration upstream of the fabric was 1500 ppm; downstream of the fabric 1100 ppm of SO_2 was measured. The overall SO_2 removal through the entire system was about 54 percent.

Several of these injection tests were conducted at different approach temperatures; an example of some of these results is illustrated in Figure 4. In each of the vertical bars, which symbolize the overall SO_2 removal, partitions indicate the contributions of duct, plenum and dustcake-fabric reactions. The results indicate a trend of lower removal efficiencies at higher approach temperatures. Figure 5 shows the total SO_2 removal rates vs. relative humidity for most of the tests performed with pressure hydrated dolomitic lime for a stoichiometry range from 0.75 to 1.34. The graph again indicates the trend of higher removal rates at higher relative humidities. In some of these tests (circles and triangles) no water was injected; only steam injection and heat extraction (circles) or heat extraction only (triangles) were utilized to raise the relative humidity.

Throughout each test the SO_2 concentration was monitored at the 4 sample locations previously mentioned. The 4 locations were scanned sequentially. This allowed variations in SO_2 concentration levels to be monitored as the test progressed. Figure 6 illustrates normal changes in the SO_2 concentrations at the 4 sample locations throughout a typical test. These results could be used to predict also how SO_2 removal rates would develop in a baghouse facility with periodic cleaning cycles.

Five different sorbent materials were investigated: quick lime, pressure hydrated high calcium lime, conventionally slaked hydrated lime, pressure hydrated dolomitic lime, and precalcined pressure hydrated dolomitic lime. A comparison of results of these tests at a reagent ratio between 2 and 3 are summarized in Figure 7. The The highest removal rate (78%) was achieved by precalcined pressure hydrated dolomitic lime, followed by pressure hydrated dolomitic lime (60%), conventionally slaked hydrated lime (47%), pressure hydrated high calcium lime (45%), and quick lime (23%).

SUMMARY AND CONCLUSIONS

These tests were intended to be proof of concept for all-dry sorbent injection of calcium sorbents for SO_2 emission control. Analysis of the data have led to the following conclusions:

- SO_2 and particulate removal via calcium sorbent injection upstream of a fabric filter is technically feasible.
- Removal rates of 50% were accomplished at reagent ratios of 1:1, and up to 80% at reagent ratios of 3:1.
- The relative humidity and reagent ratio appear to be the most important variables governing the removal efficiency.
- SO_2 removal occurred in the ductwork, fabric filter plenum and in the filter dustcake.
- Precalcining pressure hydrated dolomitic lime, significantly improved its reactivity (higher surface area) and SO_2 removal.

ACKNOWLEDGEMENTS

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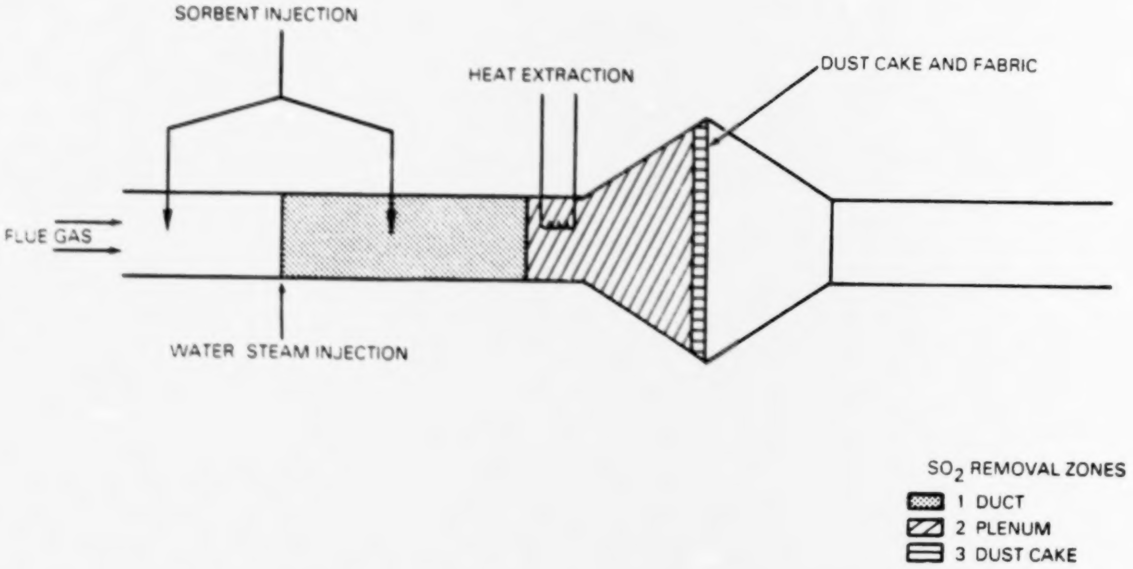
SORBENT INJECTION
HEAT EXTRACTION
DUST CAKE AND FABRIC
FLUE GAS
WATER STEAM INJECTION
SO_2 REMOVAL ZONES
▨ 1 DUCT
▨ 2 PLENUM
▤ 3 DUST CAKE

Figure 1. Schematic of SO_2 Removal Process

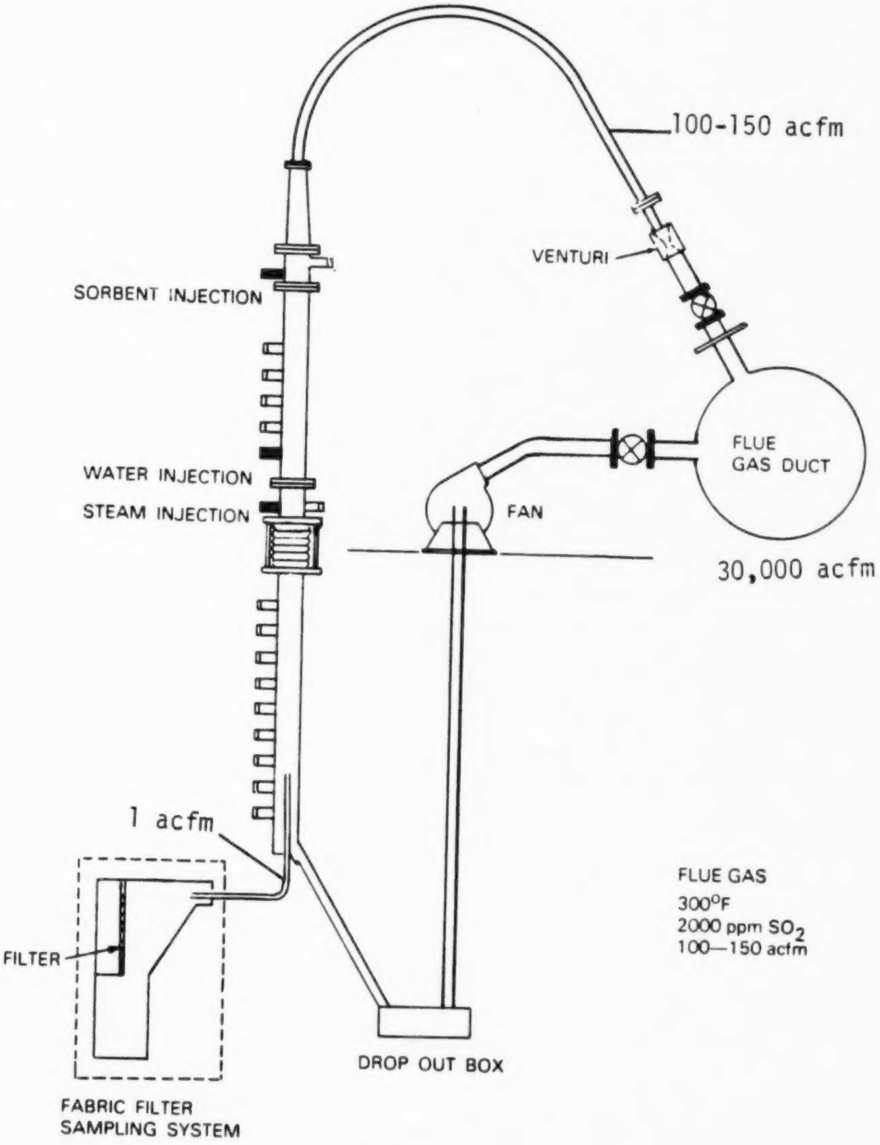
100-150 acfm
VENTURI
SORBENT INJECTION
WATER INJECTION
STEAM INJECTION
FLUE GAS DUCT
FAN
30,000 acfm
1 acfm
FLUE GAS
300°F
2000 ppm SO2
100—150 acfm
FILTER
DROP OUT BOX
FABRIC FILTER SAMPLING SYSTEM

Figure 2. Dry Injection Test Facility

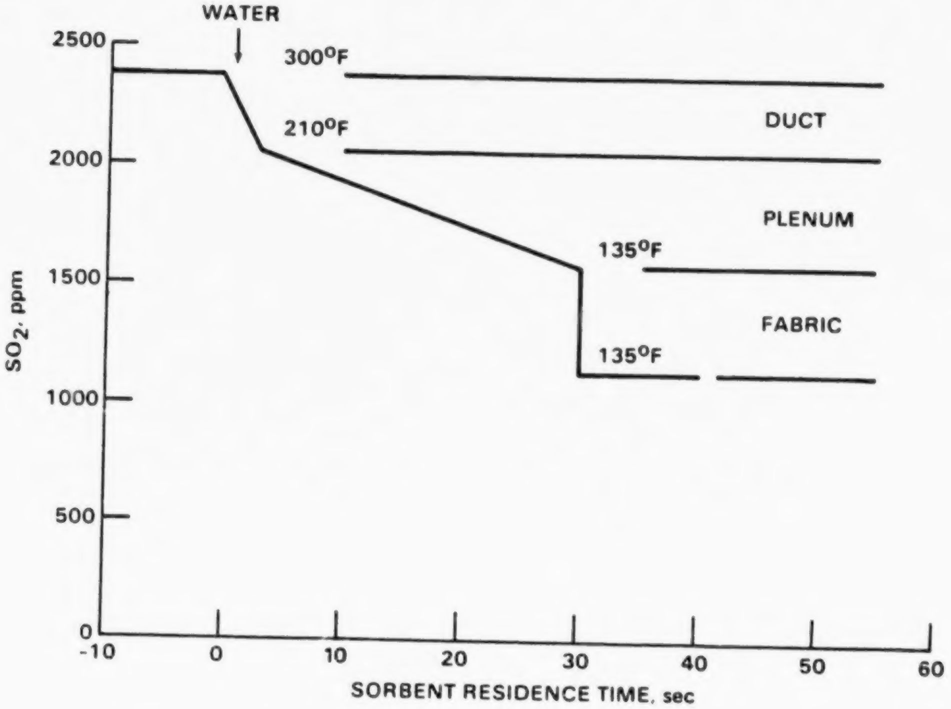

Figure 3. System SO_2 Profile with Pressure Hydrated Dolomitic Lime at a Stoichiometric Ratio of Ca/S = 1:1

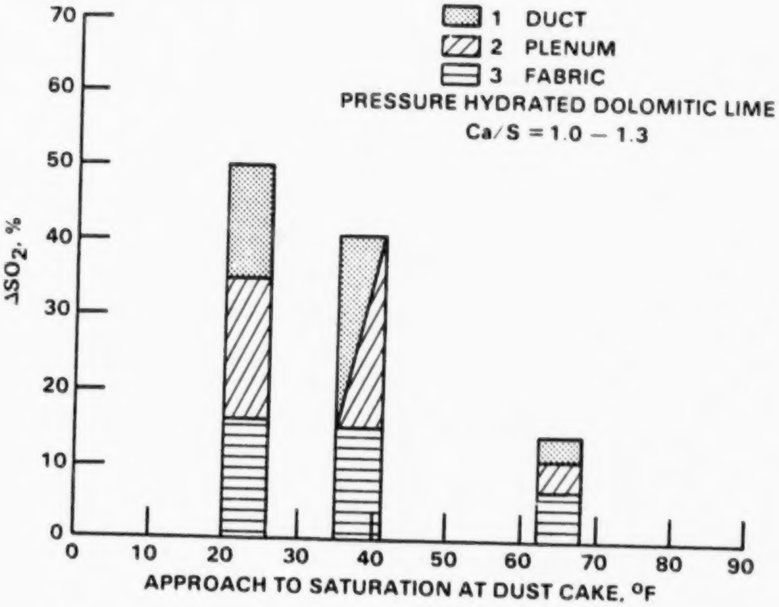

Figure 4. Contribution to Overall System Removal

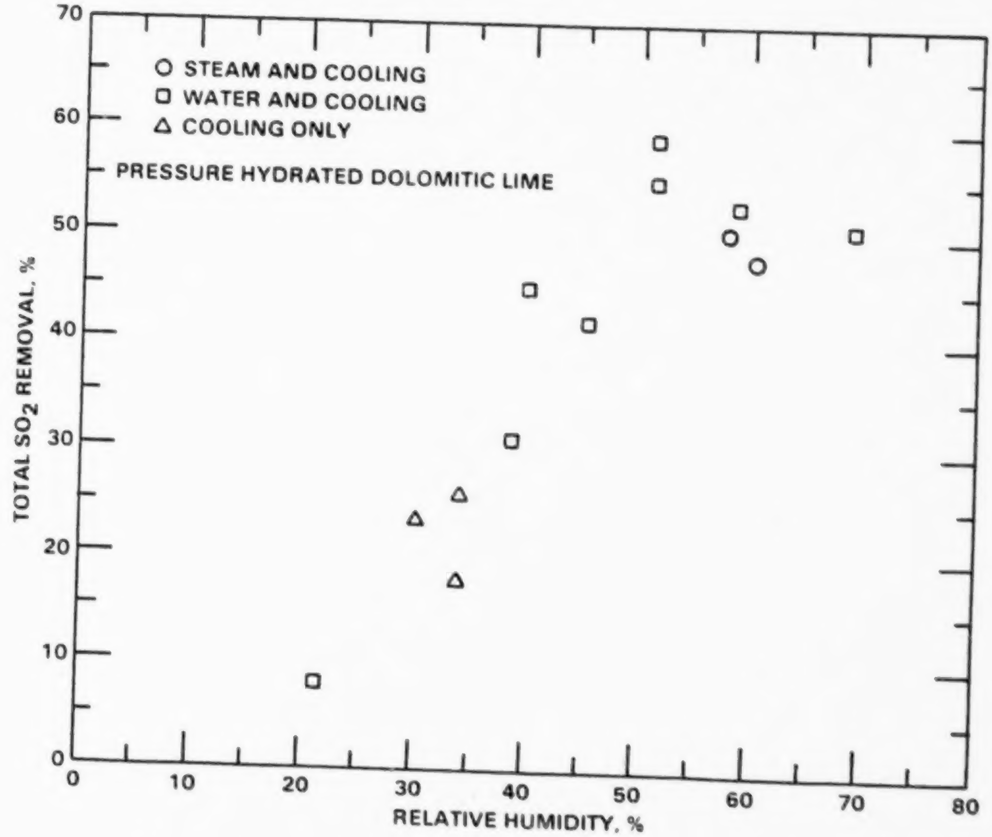

Figure 5. Total SO_2 Removal vs. Relative Humidity

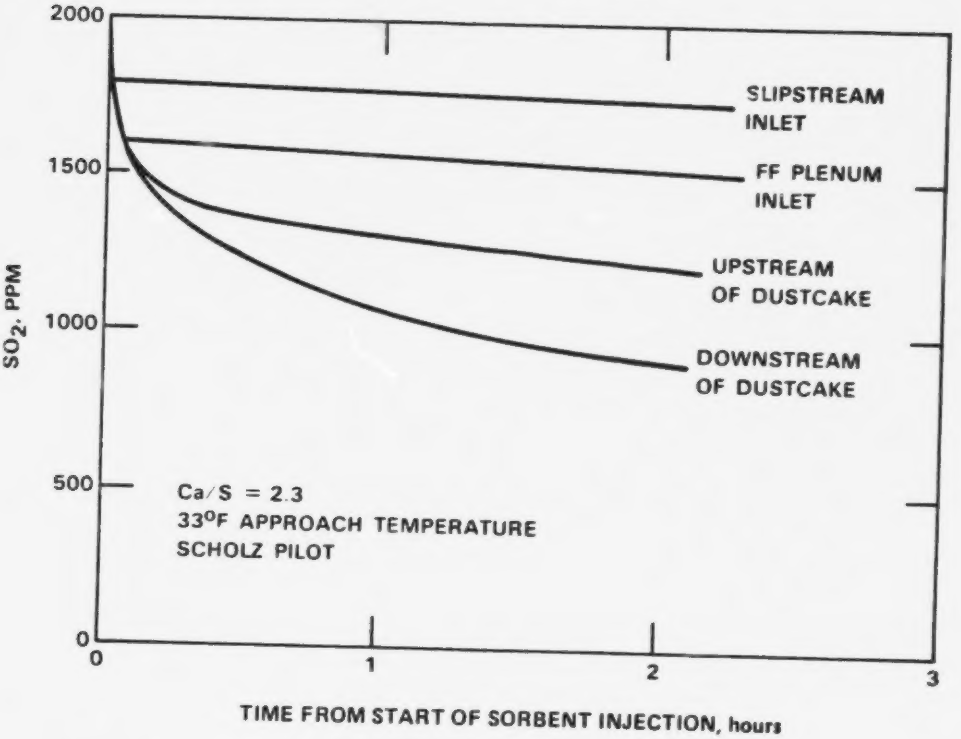

Figure 6. SO$_2$ Removal vs. Time From Start of Sorbent Injection With Pressure Hydrated High Calcium Lime

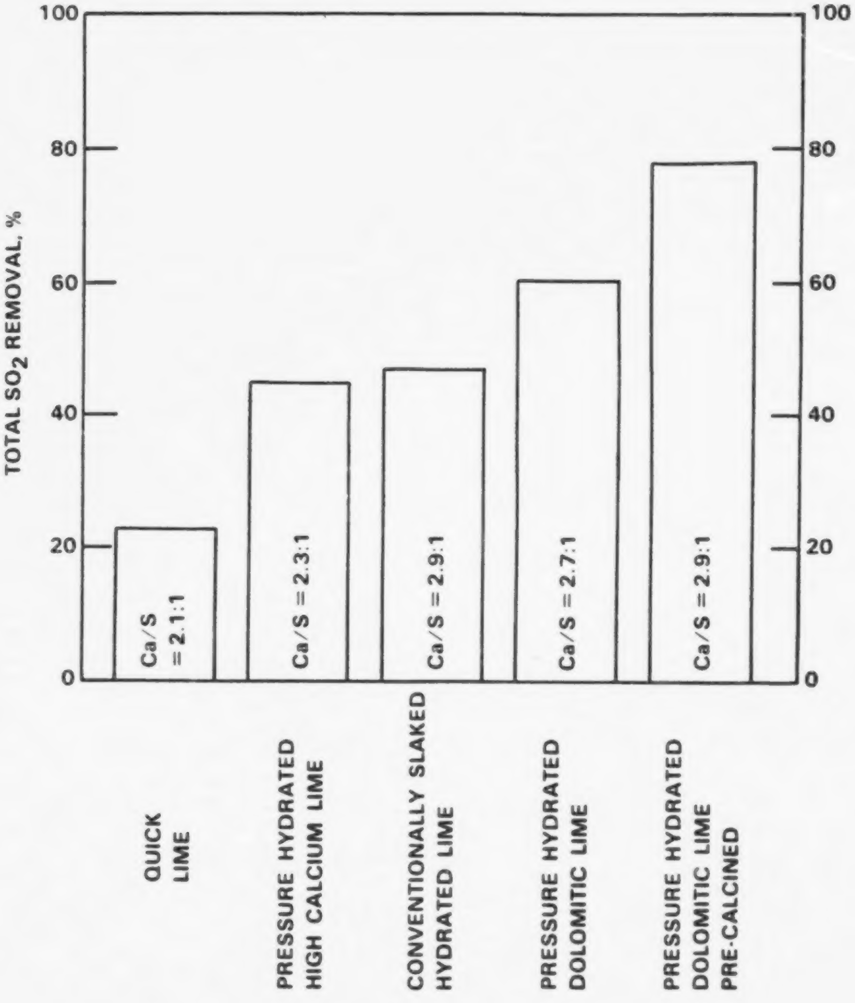

Figure 7. Total SO_2 Removal for Different Sorbent Materials